Wettability control in electrocatalytic CO₂ reduction: Effects, modulations and mechanisms

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ABSTRACT

Wettability control at the electrolyte/electrode interface represents a critical factor governing the fundamental mechanisms of reaction pathways and kinetics in practical electrocatalysis. Under an applied electrical field, a variety of physicochemical events take place at the electrolyte/electrode interface consisting of gas diffusion layers (GDL) and electrical double layers (EDL), including the transportation of kinetically relevant species, the dynamic desorption/adsorption of surface species and surface reactions. Here, using CO₂ electrocatalytic reduction (CO₂ER) as a model system, we review the fundamentals of wettability, existing and emerging means for the modulation and characterization of wettability, a molecular-level understanding of the effect of wettability at the electrolyte/electrode interface, followed by critically reviewing existing issues and future prospects of wettability control in general electrocatalysis. The review aims to systematically construct a physicochemical model of the liquid/solid interface under the influence of wettability, examining its effect on CO₂ER and general electrocatalytic systems, thereby providing insights for subsequent electrocatalytic reactions.

1. Introduction

Rapid industrialization and deforestation have led to an alarming accumulation of carbon dioxide (CO₂) in the atmosphere, reaching 400 ppm, and the associated environmental issues including energy crisis, greenhouse effect, and ocean acidification have become grave societal concerns [1]. The development of an affordable and highly efficient CO₂ fixation technique is one of the key efforts for a sustainable energy supply chain. Electrochemical reduction of CO₂ (CO₂ER) into value-added chemicals has recently emerged as one of the most promising approaches for CO₂ fixation [2]. On one hand, CO₂ER can utilize inexpensive and clean electricity generated by solar energy, hydroelectric power, and wind power, converting electrical energy into chemical bonds of energy carriers [3]. On the other hand, from a practical application standpoint, CO₂ER can achieve precise control of product distribution and reaction kinetics under mild conditions, i.e., near room temperature and ambient pressure, simply by manipulating the applied potential across the two electrodes under ambient conditions [3]. Consequently, CO₂ER enables highly selective and economically

efficient production of value-added chemicals, two key factors for mass-scale applications [4].

With a standard Gibbs free energy of − 394.4 kJ/mol, CO₂ is highly stable under ambient conditions and its reduction is characterized by a multistep, multi-electron transfer, and kinetically sluggish process. High energy barriers result in slow reaction kinetics, complex mass transfer processes (involving reactants, products, and reaction intermediates), and multiple pathways, leading to a wide distribution of products and low reaction rates [5–9]. Under industrially relevant operating conditions, the economic production of value-added chemicals becomes a priority, requiring significantly enhanced reaction rates, i.e., higher current densities, and stability of the electrolytic cell, particularly robust performance of the electrocatalysts under harsh conditions.

Wettability at the electrolyte/electrode interface represents a critical but less explored, or even neglected field due to its complexity and lack of characterization means. In fact, it governs the fundamental mechanisms of reaction pathways and kinetics in CO₂ER. Wettability inevitably influences the gas diffusion layer (GDL) and electrical double layer (EDL) between reactants and electrodes. Tuning the wettability of the

electrode can directly affect the transportation of kinetically relevant species and reaction dynamics of underwater gas bubbles, altering the equilibrium of desorption/adsorption of surface species [10]. Under specific conditions, particularly when reaction rate at the electrolyte/electrode interface is faster than the diffusion of reactants towards the electrode, mass transport dominates reaction kinetics and even reaction pathways. For instance, undersaturated CO_2, even at low current densities such as 10 mA/cm^2, leads to preferential formation of hydrogen evolution reaction (HER) over CO_2ER [11]. The coverage of kinetically relevant surface intermediates heavily depends on the mass transport of CO_2, where the binding energies of these surface intermediates vary as a function of their respective coverages, which ultimately lead to the formation of different products (reaction pathways) [12] and reaction kinetics [13–15]. Therefore, the wettability of the electrode surface significantly impacts the outcome of CO_2ER.

Modulation of wettability offers the potential to serve as an additional means to tune the selectivity and reaction kinetics of CO_2ER while also maximizing its stability and lifetime under large current densities [16]. It is important to note that CO_2ER encompasses both gas evolution reactions (GER) and gas consumption reactions (GCR), with the hydrogen evolution reaction (HER) acting as a competitive GER [17]. The complex electrolyte/electrode interface under CO_2ER conditions highlights the significant role of wettability in the outcome of electrocatalytic reactions. For instance, a hydrophilic surface facilitates the transportation of gaseous reactants in GCR, while gaseous products desorb easily from a hydrophilic surface in GER. Consequently, wettability and the associated mass transportation directly govern the coverage and binding energy of kinetically relevant species and intermediates on a working electrode, thereby influencing the reaction dynamics of CO_2ER.

A variety of approaches have been employed to modulate and characterize wettability at the electrolyte/electrode interface in CO_2ER [18]. For instance, super-wettability can be achieved by adjusting the surface chemistry using chemical methods, such as coating with hydrophobic polymers [29]. Similarly, wettability can be manipulated to attain the desired super-wettability by designing specific micro-nano morphologies through regulating the surface micro-nano structure and altering the surface roughness [19,20]. Biomimetic strategies that integrate the aforementioned approaches, achieved through careful design, have also been utilized to tune surface wettability [15,29,30]. Recently, new strategies, including 4D printing [20,21], various thin film deposition techniques [22,23], nanoimprint lithography [24,25], and laser direct writing [26–32], have demonstrated appealing potentials in manipulating surface wettability through diverse physical and chemical means, as further detailed below.

Conventionally, surface wettability is qualitatively evaluated using the contact angle tests [33]. However, a more comprehensive understanding of the microscopic details at the three-phase interface of CO_2ER, particularly the chemical, structural, and electronic properties under electrically polarized conditions, is essential for thoroughly elucidating the role of wettability in electrochemical systems. To grasp the reaction mechanism and to effectively regulate electrocatalytic performance, researchers have investigated the effect of wettability on CO_2ER using various tools, including X-ray absorption spectroscopy (XAS) [34], X-ray photoelectron spectroscopy (XPS), and vibrational spectroscopies (Raman and infrared spectroscopies [35–37]. Several in-situ/*operando* techniques, such as ambient pressure XPS (APXPS), attenuated total reflection infrared spectroscopy (ATR-IR), and scanning electrochemical cell microscopy (SECCM) [38–40], have been employed to study gas/liquid/solid three-phase interfaces for mechanistic insights.

In this review, we aim to elucidate the relationship between the wettability of a working electrode and the electrocatalytic performance of CO_2ER. First, we summarize the theoretical fundamentals of wettability and systematically review the modulation and currently available characterization methods of wettability. Additionally, we critically discuss existing issues and future prospects concerning the effect of wettability in CO_2ER. This review aims to systematically construct a physicochemical model of the liquid/solid interface, examining the influence of wettability on CO_2ER and general electrocatalytic systems, thereby providing insights for subsequent electrocatalytic reactions. Fig. 1.

2. Fundamentals of wettability

2.1. Static wetting

The fundamental principles of wettability have been comprehensively investigated. Here we primarily focus on the essential aspects of wettability relevant to CO_2ER [41–44]. In flow cell-based CO_2ER, the wettability of the gas-liquid-solid three-phase interface has not been systematically examined at a molecular level. Intramolecular forces, including van der Waals and electrostatic interactions, dictate whether a liquid can wet a solid surface [45]. The well-established Young's model is commonly employed to assess the wettability of a solid surface, as depicted in Fig. 2. The contact angle can be determined from the surface tension at the three-phase interfaces when the droplet is situated on an ideal plane (structurally and chemically homogeneous) [45].

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \tag{1}$$

where θ is the intrinsic contact angle of the liquid ; γ_{SV}, γ_{SL}, and γ_{SL} stand for the interfacial tension at the solid-vapor, solid-liquid, and liquid-vapor interfaces, respectively.

However, Eq. (1) is generally applicable only to ideal surfaces. Given that the electrocatalyst surface in CO_2ER is typically rough or exhibits chemical inhomogeneities, Eq. (1) fails to yield reasonably accurate results. Consequently, researchers introduced the Wenzel state, Cassie-Baxter state, and Wenzel-Cassie coexistence state to characterize the wetting state of a liquid on a rough surface [46]. Initially, when the protrusions between the rough surfaces are coated with liquid, Eq. (2) accounts for the relationship between the apparent contact angle and the intrinsic contact angle under Wenzel conditions. It is evident from Eq. (2) that when material surface is hydrophilic, $r \cos \theta$ decreases monotonically between $\pi/2$ and π and decrease further as r increases, leading to increased., i.e., more hydrophilic. When the droplet is positioned on an air-and-solid composite surface, Eq. (3) can be employed to describe the relationship between the apparent contact angle and the intrinsic contact angle. It is important to note that the two models discussed above are only effective when the droplet is significantly larger than the microstructure of the catalyst surface [47].

$$\cos \theta_W = r \cos \theta \tag{2}$$

$$\cos \theta_{CB} = f \cos \theta + f - 1 \tag{3}$$

Where θ_W, θ_{CB} are the apparent contact angles; r is the material's surface roughness factor; and f is the proportion of solid to porous surfaces.

The influence of wettability on the reaction mechanisms of electrocatalytic systems at the electrolyte/electrode interface has been explored [15,16,48]. As an example, factors affecting the electrode polarization current in an electrochemical reaction is as follows [49],

$$i_l = zFD \frac{C*}{\delta} \tag{4}$$

where z is the number of electrons associated with reaction, F is the Faraday constant, D is the diffusion coefficient, $C*$ is the concentration of the electroactive substance in the bulk electrolyte and δ is diffusion layer of thickness.

Eq. (4) demonstrates that the current density limit is inversely proportional to the diffusion layer's thickness. The primary products of CO_2ER include CO (g), HCOOH (l), CH_4 (g), CH_3OH (l), C_2H_4 (g), C_2H_5OH (l), C_3H_7OH (l), and others, involving intricate gas-in/gas-out and gas-in/liquid/out environments. When the product is a gaseous
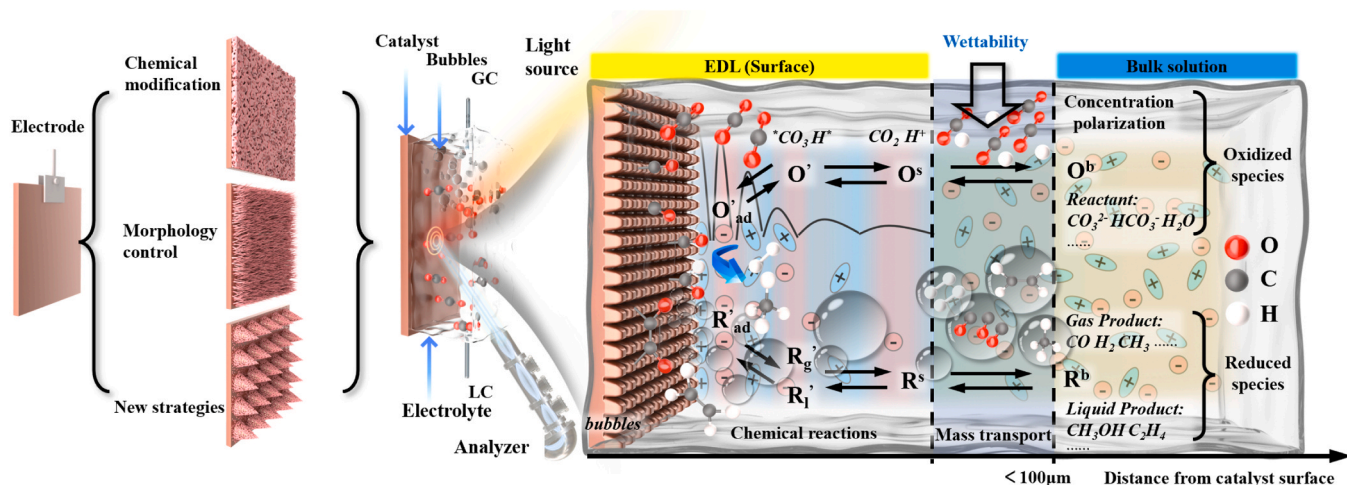
Fig. 1. Effects of wettability on different surfaces in CO$_2$ER and a qualitative description of the physicochemical details of the liquid/solid interface.
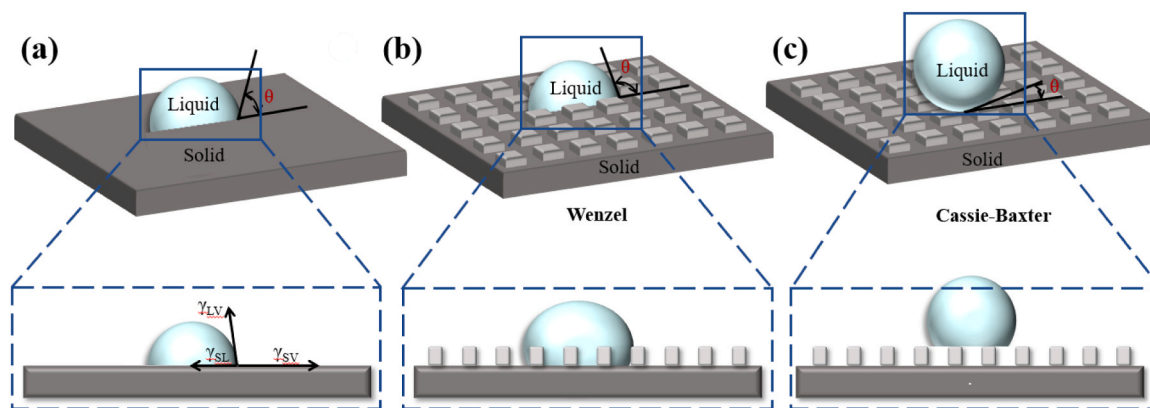

Fig. 2. Contact angles on different states (a) ideal plan; (b) Wenzel wetting state; (c) Cassie-Baxter wetting state.

molecule, the diffusion layer's thickness is equal to the gas layer's thickness adjacent to the catalyst interface. Since the catalyst surface's wettability affects the adhesion of reactant/product bubbles and subsequently the diffusion layer's thickness, the current density increases as the diffusion layer's thickness decreases [15]. Consequently, by adjusting the electrodes' wettability to hydrophilic or superhydrophilic states, the transfer efficiency of gaseous reactants can be enhanced [18]. When the product is in liquid form, the impact of gas-consumption and gas-release behaviors is crucial for the reaction kinetics and outcome of CO$_2$ER, where the electrode's structural and surface chemical properties play a vital role.

2.2. Wetting under electric field

It has been recognized that rates of industrial-scale electrolysis are unattainable in conventional H cells due to CO$_2$ mass transport limitations. The rapid development of flow cells combined with gas diffusion electrodes (GDEs) has emerged to address CO$_2$ transport constraints and significantly accelerate the reaction kinetics. Under the influence of an external electric field, an EDL forms at the electrolyte/electrode interface [50]. In the context of CO$_2$ER, the applied electric field drives liquid diffusion and wets the catalyst surface [51]. It has been discovered that electrowetting is more readily achieved on conductive materials than on dielectrics. Consequently, dielectric hydrophobic materials are incorporated into the CL to help maintain the primary liquid-solid reaction zone and the gas phase channel [52–54].

Three primary mechanisms have been proposed to elucidate the

significant impact of the electric field on electrode wettability: 1) redistribution of interfacial charges and the associated modification of solid-liquid interfacial interactions; 2) amplification of liquid movement within solid pores driven by electrochemical capillary pressures; 3) alteration of the local physicochemical environment, which is closely related to electrode wettability.

Eq. (5) can be used to define the statistical relationship between contact angles and applied potentials [41].

$$\cos \theta_E = \cos \theta_0 + \frac{1}{2} \frac{\varepsilon \varepsilon_0}{\gamma_{LV} d} (E - E_{PZC})^2 \tag{5}$$

where θ_E is the contact angle under applied electric field E; E_{PZC} stands for potential of zero charge; θ_0 is the contact angle in the absence of an EDL; ε_0 is the permittivity of the free space; ε is either the dielectric constant of the layer if the electrode is covered with a dielectric layer or the dielectric constant of liquid on an electrically conductive substrate; d is the thickness of the double layer or the dielectric layer, typically decreases with an increasing ion concentration. Eq. (5) illustrates that the PZC, a condition with no excess charge, exhibits the highest hydrophobicity at the solid-liquid interface. Surface structural modifications and manipulation of functional groups can alter the E_{PZC} [55,56]. Positive or negative PZC used here is in reference to the potential of the reference electrode used in the measurements. A positive PZC intensifies the interfacial electric field, promoting CO$_2$ adsorption and the charge transfer process. Moreover, it enables the liquid to flow more easily over the solid surface, as a negative potential is required for the cathode in CO$_2$ER [57,58].

$$\text{ECP} = \frac{l}{A}\frac{\varepsilon\varepsilon_0}{d}(\text{E} - E_{\text{PZC}})^2 \tag{6}$$

The mechanical force arising from the non-uniformity of the electric field is characterized by electrochemical capillary pressure (ECP) [59]. Consequently, one factor contributing to electrolyte permeability may be the ECP generated within the CLs and microporous layers (MPLs). Furthermore, the OH⁻ produced by the cathode tends to combine with CO_2, forming less soluble salts (porous and hydrophilic) that increase capillary pressures and draw more water into the GDE pores, accelerating electrolyte flooding [52,53]. Both liquid and solid phases undergo changes when exposed to electric fields. For example, factors such as pH, local concentrations and distributions of cations, anions, and the behavior of electrolyte molecules in the liquid environment can all dramatically change under CO_2ER conditions. These factors can significantly influence the wettability of the catalyst layer. Additionally, the electrolyte percolation within the electrode structure may be affected by the overall charge under CO_2ER conditions.

Presently, GDEs are commonly employed in CO_2ER, and the ideal wetting conditions for GDEs are proposed based on the above-mentioned theoretical and experimental findings. To facilitate rapid gas transport between the CL and the gas, GDL should be designed to be gasophilic. As multiphase interactions and reactions predominantly occur within the CL, the ideal wetting conditions for CL should ensure effective transport of liquids and electrons, maximize CO_2ER activity and selectivity sites, and enhance the local environment of the catalyst.

3. Methods in the manipulation of wettability in electrocatalysis

Wettability plays a crucial role in determining reaction kinetics and even product distribution in electrocatalytic reactions, including oxygen evolution reaction (OER) [60], hydrogen evolution reaction (HER) [48,61], oxygen reduction reaction (ORR) [62], and CO_2ER [18,63]. Manipulation of wettability is typically achieved by tuning surface morphological and chemical properties through chemical modification, morphological control, or a combination of these approaches. Moreover, recent advancements such as 4D printing [21], ultrafast laser processing [32], pulsed-laser deposition (PLD) [22], and nanoimprint lithography [24] have shown great promise in manipulating wettability and can potentially be applied to CO_2ER and electrocatalysis in general. Table 1 summarizes typical approachees for manipulating surface wettability.

3.1. Chemical modifications

Surface coating is a well-established method for tailoring surface wettability through chemical modifications [75,76]. By altering the chemical composition of the electrode surface, surface free energy and the density/distribution of dangling bonds can be regulated. A variety of hydrophilic and hydrophobic species have been employed as surface coatings to achieve desired wettability, including polyvinyl pyrrolidone (PVP), polyvinylidene fluoride (PVDF), polyethylene (PE) [35], polytetrafluoroethylene (PTFE) [7], 1-octadecanethiol [77], fluorine-terminated silane [64], and n-butylamine [66].

Studies in literature have demonstrated the effectiveness of these surface coatings in electrocatalysis. Fig. 3a,b illustrates a superhydrophobic electrode designed by Liang et al. [35], featuring a hydrophobic layer of PVDF coated on a copper oxide (CuO) electrode, creating a diffusion-constrained environment for CO_2ER. As a result of proton consumption during CO_2ER, the local alkalinity generates hydroxide ions (OH⁻) that facilitate C-C couplings, leading to enhanced production of ethylene. Furthermore, Shi et al. [64] modified the gas/liquid/solid interface on a typical Au/C electrode using a superhydrophobic fluorine-terminated silane coupling agent (1,1,2,2-perfluorodecyl trimethoxysilane) (Fig. 3c,d). The hydrophobic design inhibits HER and tunes the selectivity of CO_2ER products. These studies suggest that modified Cu systems are sensitive to the structure of the

surrounding water molecules, which may offer new avenues for enhancing CO_2ER selectivity.

While surface coating is a frequently used, it has several disadvantages that cannot be overlooked [60]. One issue is that the chemicals used can interact with either the catalyst substrate or the CO_2ER intermediates and occupy catalytically active sites. Notably, surface coatings often lack chemical bonds with the substrate, which inevitably results in a short lifespan and low mechanical robustness. Consequently, relying solely on surface coating may not be sufficient for developing stable and efficient electrocatalysts suitable for large-scale practical applications and commercialization.

3.2. Morphology control

Micro-nano morphology control can modulate the wettability properties of solid surfaces by altering their microstructures, such as increasing roughness or designing specific microstructures [61,78]. Morphology control can effectively maintain the intrinsic catalyst properties and provide stability to the catalyst while simultaneously altering local CO_2 concentration [79], facilitating adsorption/desorption dynamics of active surface species [80], creating pH gradients [81], improving wettability [82], and enhancing mass transport [18]. In the context of CO_2ER electrocatalysis, gas bubbles and liquid products often cover the electrocatalyst surface, leading to reduced mass transfer and blockage of active sites [48]. However, it has been demonstrated that micro/nano-engineering of the catalyst surface can help minimize the negative effects of gas bubble adhesion and create a low-adhesion electrode, providing a promising approach for optimizing CO_2ER electrocatalyst.

Niu et al. [19] reported the development of a bio-copper catalyst integrated into a GDL (Fig. 3e,f), emulating the distinctive hierarchical structure of hydrophobic dogwood leaves. The layered copper structure confers sufficient hydrophobicity to the electrode for CO_2 reduction, creating a robust gas-liquid-solid three-phase boundary. This boundary traps more CO_2 near the active copper surface and resists electrolyte repulsion, even during high current density operations. In a related study, Burdyny et al. [68] investigated the electroreduction of CO_2 to CO in an aqueous electrolyte, considering the impact of gas consumption and gas release behavior on critical reaction parameters. Using Au as an example, the team examined the morphological effects of electrode shape on gas release behaviors during CO_2ER. Comparing nanopins, nanorods, and nanoparticles, researchers found that these morphological differences enhance the long-range transport of CO_2, removing mass transfer limitations encountered by the catalysts at a current density of ~20 mA-2/cm. Wicks et al. [20] reported the development of 3D printable fluoropolymer GDLs with adjustable micropores and structures, where the effects of permeability, microstructural porosity, macrostructure, and surface morphology on the performance of GDL were investigated. Notably, a remarkable high current density due to the creation of pyramidal macrostructures was observed. All these findings suggest a promising pathway to improve the CO_2ER GDE as a platform for 3D catalyst design.

While micro-nano morphology control has shown promising potential in the manipulation of wettability, further investigation is required due to the complexity of the interfacial environment, possible disruption of the micro-nano morphology under catalytic operating conditions, and the instability of certain hydrophilic structures. Furthermore, the modulation of wettability achieved by micro-nano morphology control is limited by the inherent wettability properties of the electrode materials. A deeper understanding of the interfacial dynamics and stability of microstructures is essential to fully realize the potential of micro-nano morphology control. Novel approaches for optimizing the micromorphology of electrode surfaces while maintaining their stability during catalytic reactions should also be explored.

Table 1
Typical methodologies in the manipulation of surface wettability and their characteristics in CO_2ER.

Methods	Advantages	Disadvantages	Example	Wettability	Electrochemical performance	Ref.
Chemical modification	Versatile; suitable for large-scale production; precise control of wettability; supporting the transport process; biocompatibility; improved adhesion.	Surface chemical contamination; possible blockakge of catalytically active sites; poor stability (lack of strong chemical bonds againse wearing); sensitive towards preparation details.	PVDF coated CuO	Hydrophobic	The activity, selectivity, and stability of CuO-based electrodes towards C_2H_4 production are enhanced.	[35]
			PTFE modified Cu nano-arrays	Hydrophobic	Boosting the Faradaic efficiency of liquid products by 67% and decreasing H_2 production by 50%.	[7]
			Fluorine-terminated silane coupling agent modified Au/C	Hydrophilic to hydrophobic	J_{CO} gradually increases as the catalyst layer becomes more hydrophilic.	[64]
			Various protic species and hydrophobic species modified Cu	Hydrophilic and hydrophobic	Hydrophilic species enhance the formation of formic acid, and cationic hydrophobic species promotes CO selectivity.	[65]
			Hydrophobic Cu/ Cu_2O sheet catalyst with hydrophobic n-butylamine layer attached	Hydrophobic	FE_{C2+} of CORR could reach 93.5%, with high current density and stability.	[66]
			Cu with controllable interficial wettability	Superhydrophobic	A C_{2+} Faradaic efficiency of 80.3% can be achieved with a high C_{2+} partial current density of 321 mA cm^{-2}, among the highest at such current densities.	[67]
Morphology control	Excellent stability; more exposure of catalytically active sites; mo chemical alteration on surface; biocompatibility; good tunability.	Difficulties in achieving large-scale production and high repeatability; material restricted; reconstruction or surface chemistry modifications in reaction; difficulties in cleaning and maintenance.	Bio-copper catalyst with hierarchical structure on a gas diffusion layer	Hydrophobic	ESCA-normalized current densities increase.	[19]
			Nanopins, nanorods and nanoparticles of Au	Hydrophobic	Achieving simultaneously high selectivity and current density of C_2 products.	[68]
			3D printable fluoropolymer Cu coated GDLs	Hydrophobic	A 1.8 × increase in the C_2H_4 partial current density.	[20]
			Au nanoparticles immobilized on a superhydrophobic porous carbon substrate	Superhydrophobic	The partial current density of CO increased by 240% from 8 °C to 60 °C; interfacial CO_2 concentration of the three-phase electrode is 26.2 times higher than that of the two-phase electrode at 60 °C.	[69]
			Cu dendrites with an ultrastable $Cu^{\delta+}$ state and hydrophobicity	Hydrophobic	Cu CF exhibited a C_2 FE of 90.6% at a partial current density of 453.3 mA cm^{-2} in a flow cell. A 400 h stable electrolysis at 800 mA and even a ground-breaking stable operation at a large industrial current of 10 A in the membrane electrode assembly (MEA) form.	[70]
Chemical modification & morphology control	Precise control of reaction pathways; modulated reaction kinetics; high energy efficiency; high selectivity.	Difficulties in design and fabrication; high cost; complex chemical composition; partly blocking active sites; diffcult for large-scale production.	Cu dendrite electrode treated by 1-octadecanethiol	Hydrophobic	A 56% Faradaic efficiency for ethylene and 17% for ethanol at neutral pH, compared to 9% and 4% on a hydrophilic, wettable equivalent.	[71]
			3D heterojunction with Cu-based catalysts	Hydrophobic	The catalyst is not constrained by prior gas-ion-electron transport restrictions, which can extend gas and ion transport from tens of nanometers to the micrometer scale.	[72]
			Alkali resistant copper electrode	Hydrophobic	70%FE of reducing CO to ethylene, operational	[73]

Table 1 (*continued*)

Methods	Advantages	Disadvantages	Example	Wettability	Electrochemical performance	Ref.
					stability and constant ethylene selectivity.	
			Femtosecond laser shaped superhydrophilic electrode	Superhydrophilic	High level of activity and stability at a current density of 10 mA cm^{-2} for 72 h.	[30]
			Hydrothermal and PTFE modified N-Doped CNTs	Hydrophilic and Hydrophobic	A 95.6% FE$_{CO}$ at -1.4 V vs Ag/AgCl with a total current density of 4.56 mA cm^{-2}.	[74]
			Spatially shaped femtosecond laser treated Janus copper foam	Superhydrophilic−Superhydrophobic	The SHL−SHB surface (3.15 g cm^{-2} h^{-1}) outperformed the other surfaces with respect to fog collection.	[31]
New strategies	Excellent patterning; multi-scale design; universal processing capabilities, especially in hard-to-process materials.	Lack of applications in electrochemistry; difficulties to apply in eletrodes.	Femtosecond laser processed electrodes	Superaerophobic	High electrochemical surface area.	[32]
			PLD treated micro/nano hierarchical structures	Superhydrophobic	The CR-SAS can be maintained ice free even under an ambient environment of -50 °C ultra-low temperature and extremely high humidity (ice supersaturation degree of ~260).	[22]
			SAL/SAB cooperative strategy on Pt electrode	Superaerophilic/superaerophobic	Ultrahigh current density at an overpotential of -500 mV.	[23]
			Nanoimprint lithography structured substrates	Superhydrophobic	More than 1000 abrasion cycles could be tolerated, 10 times higher than for conventional superhydrophobic surfaces.	[24]
			3D membrane/catalytic layer (CL) interface and gradient tapered arrays by the nanoimprinting	Hydrophobic	Increases the electrochemical active area by 4.2 times but also decreases the overpotentials of both mass transport and ohmic polarization by 13.9% and 8.7%.	[25]
			4D-printed metamaterials	Superhydrophobic	Improvement in signal-to-noise ratio (SNR) and sensitivity (S).	[21]

Note, wettability contributes to the enhanced electrochemical performance in the studies, may or may not be the major factor

3.3. Multi-strategies

Micro-nano morphological and chemical regulation methods possess distinct advantages, rendering their combination particularly appealing for comprehensive wettability manipulations. A multi-strategy approach entails the combined application of micro-nano structures to tailor surface morphological properties, expose more active sites, and modulate atomistic connectivities. This leads to the fabrication of electrocatalysts with precisely engineered surface physical and chemical properties.

By designing catalysts with tailored wettability, properties such as electrocatalytic selectivity, stability of catalysts, and electrochemical efficiency can be effectively modulated. Wakerley et al. [71] explored the wettability of Cu dendrite electrodes, inspired by spider stratum corneum structures, to understand its effect on product selectivity in CO$_2$ER. The Cu dendritic array catalyst was prepared using aqueous electrodeposition procedures, resulting in a highly roughened surface. This surface was then treated with 1-octadecanethiol to create a superhydrophobic surface. Upon wettability optimization, an increase in CO$_2$ concentration at the electrode interface was observed, compared to untreated surfaces, leading to improved CO$_2$ER selectivity. In a separate study, Dinh et al. [73] designed an alkali-resistant electrode and optimized CO$_2$ diffusion to the catalytic site by sandwiching the reaction interface between distinct hydrophobic and conductive carriers. The catalyst deposited on the GDL significantly increased the local concentration of CO$_2$. Hydroxide ions on or near the copper surface were found to reduce the activation barriers for CO$_2$ reduction and CO coupling. Furthermore, the introduction of a polymer-based GDL enhanced operational stability and maintained consistent and efficient ethylene selectivity over extended operating durations. This illustrates the design of optimized alkali-resistant electrodes, emphasizing the importance of optimized wettability and mass transfer for enhancing efficiency and selectivity in CO$_2$ER.

While the multi-strategy approach has significant potential for producing more efficient catalysts, the complex physical and chemical properties at the electrolyte/electrode surface complicate the elucidation of the working mechanism at molecular or atomistic levels, particularly under operating conditions.

3.4. New strategies

Some CO$_2$ER processes have employed the aforementioned mentioned methods to tune wettability at the electrolyte/electrode interface. However, as will be covered in greater details below, there are other emerging promising techniques for the manipulation of wettability in CO$_2$ER and electrocatalysis. We aim to expand the range of strategies for controlling the wettability in CO$_2$ER by introducing several unique, as-yet-unproven techniques for tuning wettability in electrocatalysis.
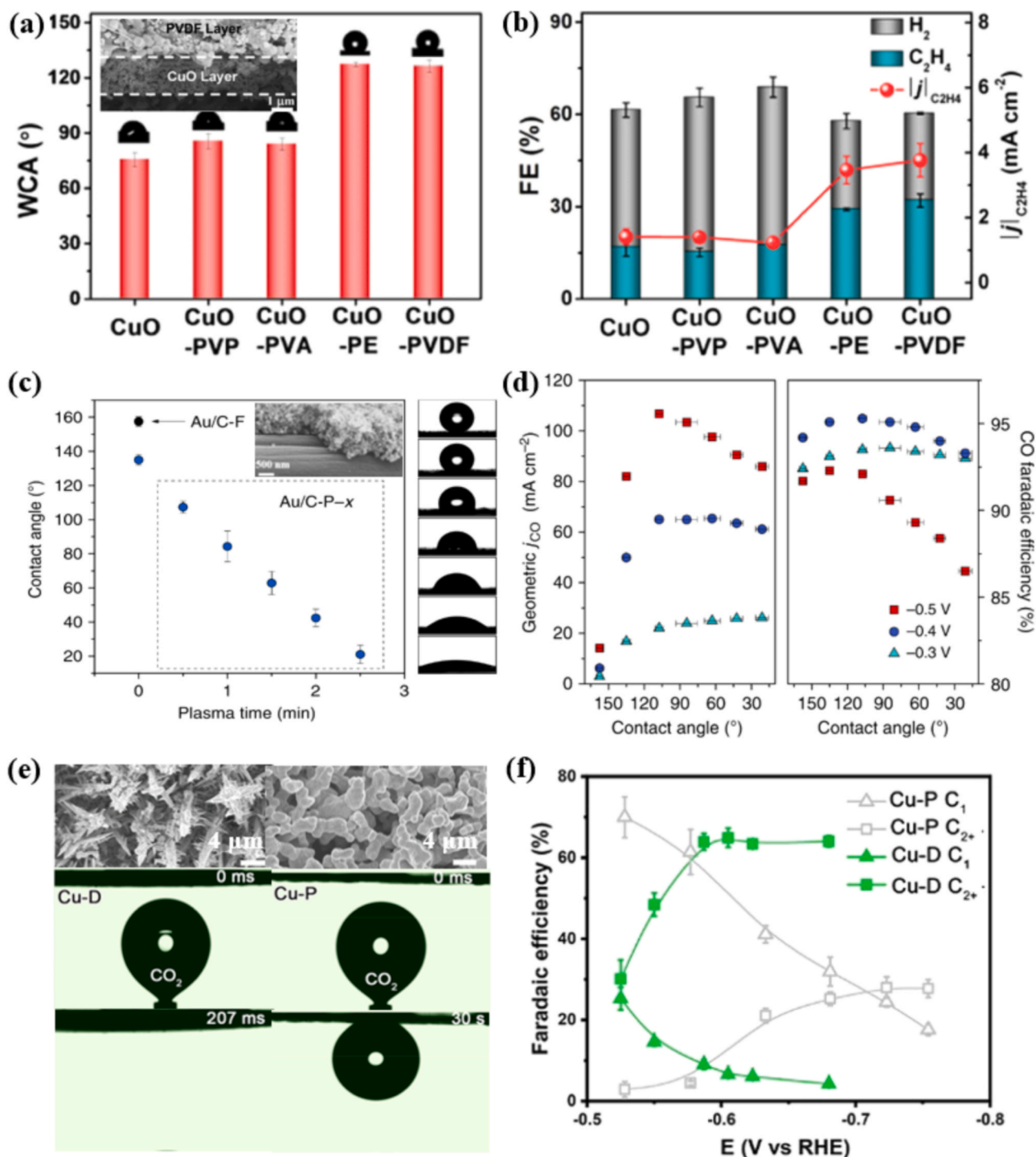
Fig. 3. Water/gas contact angles, faradaic effiency (FE) and current density (j) of electrodes tuned by different traditional wettability manipulation methods: (a) Water contact angles for CuO electrodes before and after modification using PVP, PVA, PE, and PVDF and (b) values of FE and $|j|C_2H_4$; (c) A plot of average water droplet contact angles on different Au/C electrodes and photographs of water droplets on each electrode and (d) Geometric jCO and CO Faradaic efficiency of Au/C electrodes with various water CAs at − 0.3, − 0.4 and − 0.5 V vs. RHE. Error bars represent the standard deviation of three independent experiments; (e) CO_2 bubble adhesion experiments on electrodes under a CO_2-saturated $KHCO_3$ solution and (f) their C^{2+} and C^1 faradaic efficiencies. Reproduced with permission from Ref. [35], Copyright © 2021 American Chemical Society. Ref. [64], Copyright © 2020 Springer Nature. Ref. [19], Copyright © 2021 American Chemical Society.

3.4.1. Laser/extreme manufacturing

Laser technology has demonstrated remarkable potential in developing and manipulating material wettability by constructing specialized micro- and nanoscale structures on material surfaces, yielding a range of super-wettability properties [26–28]. Ultra-fast laser pulses possess the capacity to pattern micro and nanostructures with high precision and controllability, effectively tuning hydrophilic properties through the regulation of processing parameters with high efficiency. Laser-induced micro/nanostructures can also enhance a solid surface's natural wettability [29]. Consequently, laser-ablated surfaces often exhibit strong superhydrophilicity, necessitating additional modification with low-surface-energy chemicals to achieve superhydrophobicity [83].

Liu et al. [30] introduced a novel method to fabricate self-supported superhydrophilic electrocatalysts using spatially-shaped femtosecond

laser ablation pretreatment, which resulted in the creation of self-supported cobalt oxide electrocatalysts with hierarchical chestnut burr-like nanostructures on a copper substrate. This method enables rapid charge transfer, a large surface area with populated active sites, accelerated electrolyte diffusion, efficient catalytic components, and high conductivity. Similarly, Li et al. [31] proposed a technique for creating a superhydrophilic-superhydrophobic Janus fog collector (Fig. 4a,b) by combining a spatially shaped femtosecond laser treatment on one side (superhydrophilic) of a copper foam with a chemical replacement reaction on the other side (superhydrophobic) to control water transport behaviors. Zhang et al. [32] employed high precision and controllable femtosecond laser technology to create hierarchical micro-nano structures with superaerophobic characteristics on the surface of a silicon substrate (fs-Si). Subsequent self-supporting electrodes effectively inherited this unique super-wettability through chemical synthesis. The ultra-fast laser processing technique endowed the electrodes with robust physical structure, remarkable superaerophobic efficacy, and a high electrochemical surface area. This effective application of femtosecond laser technology paves a promising route for creating self-supporting electrodes for gas-involved reactions.

3.4.2. Deposition

Deposition techniques encompass various methods for depositing thin films, coatings, or layers of materials onto substrates such as wafers or components (electrodes). Depositing materials with desired wettability and favorable electrocatalytic properties on electrodes presents a promising approach to tune electrode wettability.

He et al. [22] developed a novel strategy to optimize photosynthetic efficiency on wheat leaves based on recent research. Utilizing ultrafast PLD technology, they effectively constructed micro/nano hierarchical structured CR-SASs, which exhibited enhanced condensate self-removal properties and efficient solar anti-icing synergistic binary effects. Condensates were removed from the surface through droplet mutual coalescence, as the unique surface nanostructural features prevented wetting of condensed microdroplets and reduced solid-liquid adhesion. In another study, Zhang et al. [23] reported a super-aerophilic/superaerophobic cooperative electrode (Fig. 4c,d) that efficiently accelerated dissolved H_2 diffusion by minimizing the diffusion distance and promoted bubble transfer through asymmetric Laplace pressure. Compared to a flat Pt electrode, the enhanced mass transfer reduced the overpotential. This SAL/SAB cooperative strategy effectively increases HER efficiency and advances understanding of various gas-involved processes.

3.4.3. Nanoimprint lithography

Nanoimprint lithography (NIL) is a high-resolution, low-cost, and versatile patterning technique for creating precise and reproducible nanoscale structures on various substrates. Super wettability can be achieved by constructing surfaces on two different length scales using nanoimprinting, wherein the nanostructure design provides the desired infiltration and the microstructure design ensures durability. This approach can be employed to design precise and reliable structures for malleable electrode materials, tuning wettability while enhancing the specific surface area.

A recent study by Wang et al. [24] demonstrates how surface structuring at two different length scales can achieve robust super-hydrophobicity. While the microstructure design enhances longevity, the nanostructure design imparts water repellency. Several substrates, including silicon, ceramic, metal, and clear glass, were employed in this method. Remarkably, even after abrasion with sandpaper and a sharp steel blade, the water repellency of the resulting superhydrophobic surfaces remained intact. The unique structure's overall design, maximizing the gradient CL, rapid mass transport, and triple-phase interface, increases the electrochemically active area while reducing the overpotentials of mass transport and ohmic polarization. Consequently, the ordered structure with Ir loading offers excellent efficiency and stability.

3.4.4. 4D printing

Surface microstructure is crucial for tuning surface wettability [84]. In most instances, the formed surface microstructure is fixed, rendering surface wettability unchangeable. However, 4D printing offers a potentially straightforward approach to create tunable surface wettability by reversibly altering the surface microstructure [85].

Nan et al. [21] proposed a shape memory sensor combining micro-level biomimetic electrodes with 4D-printed fractal-inspired meta-materials. This innovative sensor exhibits adjustable wettability and electrical performance (Fig. 4e,f) through functional and structural reconfiguration, enhanced sensitivity, and high flexibility. In addition to high sensitivity to signal feedback, the metamaterial demonstrates a remarkable capacity to reconfigure its electrical and mechanical properties in response to external stimuli. These results highlight the potential applications of 4D-printed metamaterials in the electroreduction industry. Liu et al. [84] employed a 4D printing technique based on two-photon lithography to achieve reversible, bidirectional self-assembly of microstructures. By asymmetric crosslinking density, the printed vertical microstructures can transition to a bent state with controlled thickness, curvature, and smooth morphology. This technique enables the fabrication of micron-scale structures to obtain surfaces with switchable wettability, which holds significant potential in electrochemistry.

These novel strategies for modifying wettability offers several advantages over traditional chemical techniques, including their suitability for environments with mild reactions, extended lifespans, and the integration of unique structural patterning that allows for more precise mass transport control. The final product exhibits high mechanical strength, attributable to the strategy's incorporation of chemistry and mechanics. The benefits of this approach extend beyond CO_2 electro-reduction because of its adaptability and potential applications in other fields of study.

While this review has primarily focused on methods for altering electrode surface wettability, it is crucial to consider that the reaction solution's properties also significantly influence the electrode surface wettability. Previous research [86,87] has demonstrated that reducing the liquid's cohesion can enhance surface wetting, and decreasing the liquid's surface tension can further amplify this effect.

4. *In-situ/operando* characterization of the electrolyte/electrode interface

Investigating the chemical, structural, and electronic properties of dynamically evolving gas/solid, liquid/solid, and gas/liquid interfaces is highly desirable due to the ubiquity of such interfaces in heterogeneous catalysis, electrocatalysis, and general physical science. As a fundamental phenomenon, chemical reactions occurring at the gas/liquid/solid interface are vital to industrial production and operation, and hold significant importance in addressing key challenges in their respective fields. In particular, establishing the structure-function relationship and tracking the dynamic physicochemical processes on a CO_2ER electrocatalyst surface are essential to comprehend the wett-ability's working principle. This endeavor requires the use of high-precision characterization techniques with suitable spatial and temporal resolution. Various state-of-the-art interfacial observation and characterization techniques are available, particularly spectroscopic, microscopic, and imaging methods. These approaches enable researchers to establish the relationship between a catalyst's physicochemical structures, regulatory outcomes, and the mechanisms underlying catalyst wettability modulation in CO_2ER, paving the way for the design and development of efficient and selective catalysts.

4.1. Representative spectroscopies

Probing the liquid/solid interface can be highly challenging due to its intrinsic complexity, heterogeneity, and dynamic changes under the
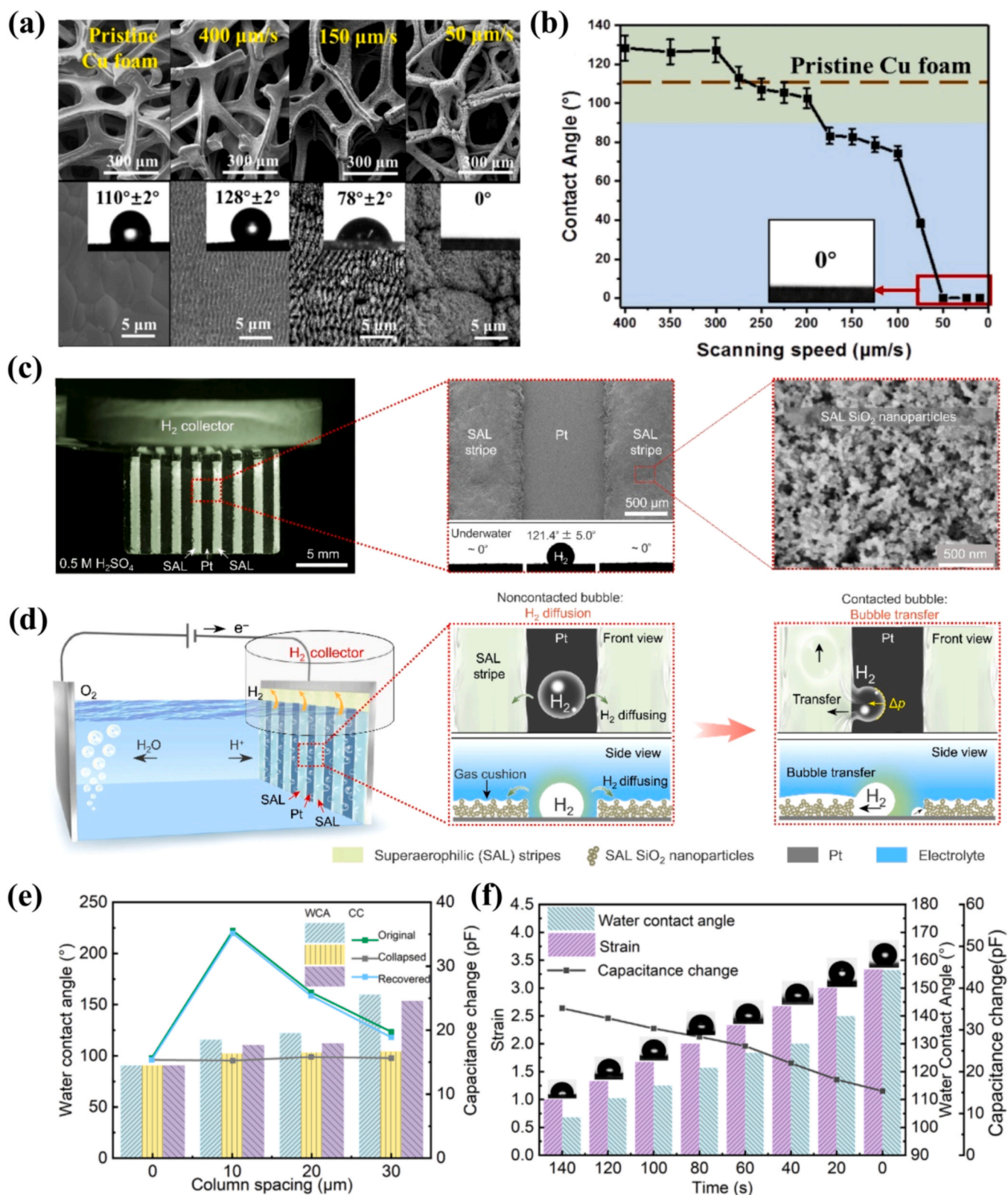
Fig. 4. New methods of wettability manipulation of CO_2ER including (a)(b) laser/extreme manufacturing; (c)(d) deposition; (e)(f) 4D printing. Reproduced with permission from Ref. [31], Copyright © 2022 American Chemical Society. Ref. [23], Copyright © 2023 The American Association for the Advancement of Science. Ref. [21], Copyright © 2022 American Chemical Society.

influence of external fields. The liquid/solid interface's importance in CO_2ER is further emphasized by the three-phase reaction system, which comprises an aqueous electrolyte, a solid electrode, and a gaseous feedstock (CO_2). Spectroscopic techniques provide a viable means of identifying, quantifying, and manipulating surface reactants, transient reactive species, and catalytically active phases at dynamically evolving liquid/solid interfaces under non-destructive and near-practical

working conditions. Here we discuss representative spectroscopic methods for investigating the effects of wettability with high spatial and temporal resolutions.

Efficient capture of photoelectrons is fundamental for photoelectron-based techniques, including APXPS. Depending on the excited X-rays' energy, the inelastic mean free path (IMFP) of outgoing photoelectrons varies from a few angstroms to tens of nanometers. To probe an H_2O/
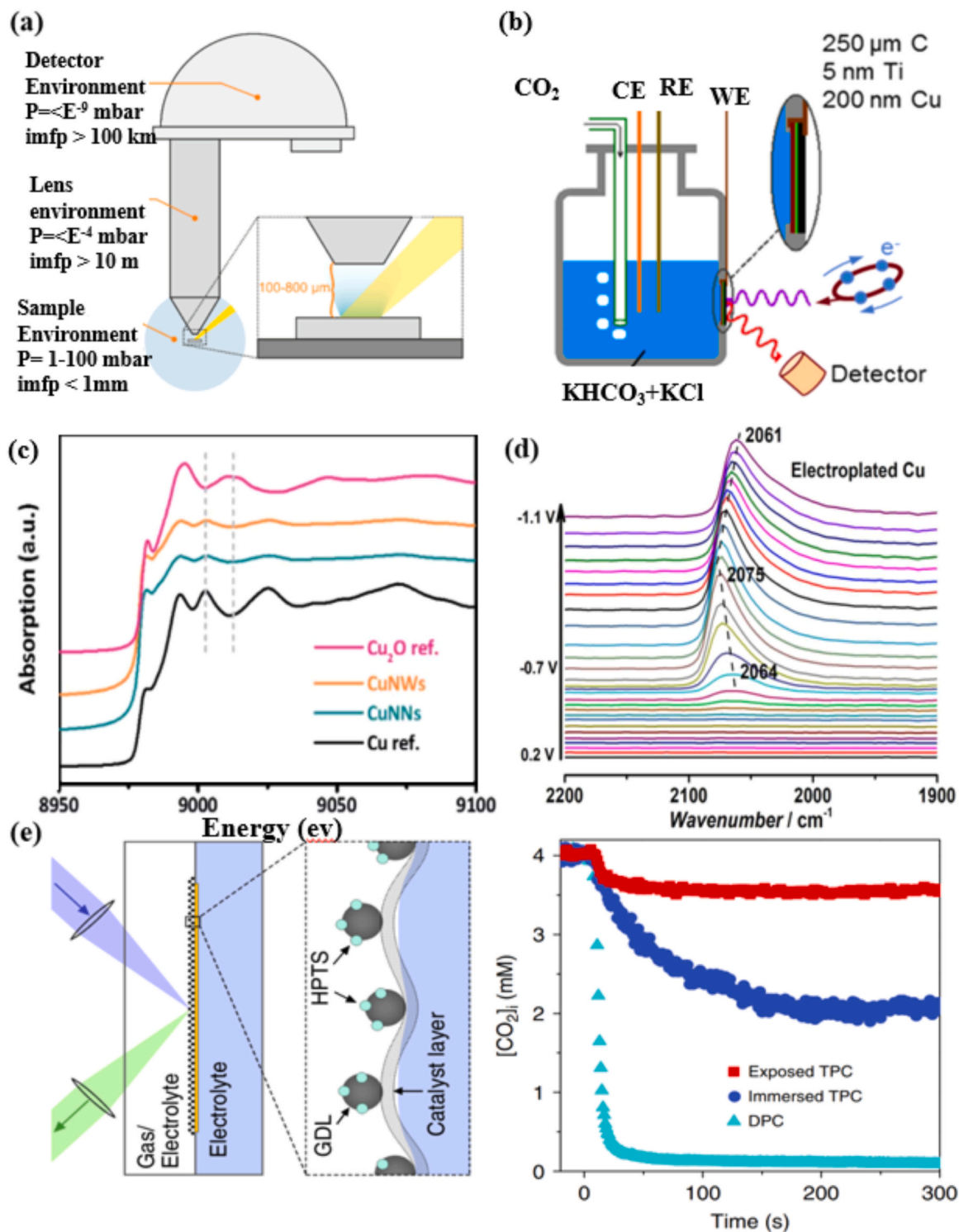
Fig. 5. Some spectral techniques (a) near-ambient pressure XPS set-up; (b) *in-situ* XAFS; (c) Cu K-edge XANES spectra of CuNNs and CuNWs after the electrochemical test (d) *in-situ* electrochemical ATR-SEIRAS spectra of CO on electroplated Cu electrodes in CO_2-saturated 0.1 M $KHCO_3$ solution; (e) schematic diagram of in situ FEM. Reproduced with permission from Ref. [108], Copyright © 2021 Wiley. Ref. [90], Copyright © 2016 American Chemical Society. Ref. [36], Copyright © 2020 Royal Society of Chemistry. Ref. [109], Copyright © 2019 Wiley. Ref. [64], Copyright © 2020 Springer.

solid interface with a substantial liquid-phase H_2O thickness and minimize signal attenuation, one can either increase the X-ray photon energy or decrease the travel distance of photoelectrons in condensed and/or gaseous media. This ensures that photoelectrons, on average, travel a distance that lies within the XPS probing depth under given conditions. APXPS is one of the most powerful means for *in-situ* observation in liquid/gas environments (Fig. 5a). As shown in Fig. 5a, the central component of an APXPS system is a reaction chamber that houses samples and allows for the introduction of vapor with pressures up to tens of millibar (mbar). The development of APXPS technology in recent years has enabled probing the solid-liquid interface under in *situ/operando* conditions. However, the probing condition must be adapted to practical liquid/solid interfaces concerning the thickness of liquid/solid layers, the presence of ions, and environmental pressures. To date, four main approaches have been developed for studying the liquid/solid interface: dip-and-pull [96,97], catalyst-coated membranes (CCMs) without graphene cover, graphene-covered holey Si_3N_4 membranes [98, 99], and CCMs with a graphene cover. The typical structure, advantages, disadvantages, and representative studies of these four methods have been reported elsewhere [100].

APXPS allows for the probe of a working electrode with a 10–30 nm electrolyte overlay [97]. By applying the dip-and-pull method, Favaro et al. probed the potential drop and the potential profile in the EDL [96]. Shavorskiy et al. used the dip-and-pull approach to investigate the band alignment at the electrolyte/semiconductor interface in a working photoelectrochemical device [40]. Yu et al. employed the dip-and-pull method for a systematic investigation of solvation and electrolyte-derived surface species at the electrolyte/Mg electrode interface [101]. In other attempts, a robust physical barrier, such as proton exchange membranes [102,103] (PEM) or silicon nitride substrates [104,105] covered by graphene top layers [104], was employed to separate a reservoir of liquid electrolyte and wet the surface of working electrocatalysts. While most studies have focused on relatively well-defined electrocatalytic systems, such as OER [96,102,103], significant promise has been demonstrated in the study of liquid/solid interfaces in CO_2ER and other more complex electrocatalytic systems

[106,107]. Specifically, as also briefly summarized in Table 2, the physicochemical processes at a liquid/solid interface can be probed using APXPS under continuously evolving conditions, including the identification of catalytically active phase, valance, atomistic connectivities and ratios of key elements, coverage of kinetically relevant surface species/intermediates that reflects wettability-driven mass transport at the electrolyte/electrode interface, and details such as distribution of reaction-relevant species and potential variation across the EDL engineered with different wettability.

APXPS holds the potential to significantly advance our understanding of wettability's role in CO_2ER. By elucidating the complex interplay between hydrophilic, hydrophobic, and catalytic properties, researchers will be empowered to design and synthesize catalysts with tailored surface characteristics to maximize reaction efficiency and selectivity. Furthermore, APXPS facilitates the investigation of dynamic alterations in surface wettability under *in-situ/operando* conditions. This enhanced mechanistic understanding will inform the development of more resilient and long-lasting catalysts for CO_2ER, ensuring their viability for large-scale deployment.

The XAS consists of distinct peaks or features that appear near the absorption edge or within the high-energy extension. The two primary XAS techniques, X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), offer complementary insights into the electronic states and atomistic connectivities of working electrocatalysts. While EXAFS can analyze local structural details such as bond length and coordination numbers around the atom of interest, XANES can reveal the electronic structure around the absorbing atoms, bond geometry, and unoccupied states density of specific elements or active sites. To monitor valence and ligand information changes in catalytic reactions and provide data to support the interpretation of catalytic mechanisms under different wettability conditions, XAS can be coupled with a custom-designed reaction cell that enables probing a dynamically evolving liquid/solid interface under *operando* conditions [34] (Fig. 5b). An et al. [36] investigated the state of hydrophobic polytetrafluoroethylene-coated copper nanoneedles (CuNNs) using XANES spectroscopy. The copper K-edge of CuNNs and

Table 2
Overview of various characterization techniques, their advantages, disadvantages and major capabilities.

Detection method	Advantages	Disadvantages	Capabilities	Ref.
In-situ IR	Suitable for monitoring the identity and dynamic evolution of equilibrated and transiently formed species at close-to practical working conditions.	Special optical devices are needed to observe the physicochemical state of catalysts; less used for quantification; weak element specificities.	1) Identifies key reaction intermediates and pathways. 2) High spatial and temporal resolution spectroscopy to track reaction dynamics. 3) Reveals a variety of physicochemical properties of the electrolyte/electrode interface.	[88]
XAFS	Analysis of amorphous materials; element-specific studies without interference; highly precise determination of structural parameters including coordination type, number, and lattice spacings.	Insensitive to lighter elements; often requires high-energy synchrotron; provides averaged structural information.	1) Identifies the catalytic reaction active sites and their evolutions. 2) Reveals the chemical environment of atoms of interest.	[89, 90]
APXPS	Enables analysis of all elements except H; offering detailed surface information in close-to realistic environments; providing real-time insights into dynamic behavior and mechanisms.	Requires ultra-high vacuum instrumentations; faces technical challenges in analyzing buried surfaces/interfaces.	1) Tracks surface composition, oxidation states and evolutions under *operando* conditions. 2) Reveals the evolution of band structures.	[91]
LP-TEM	Direct observation of dynamic processes in liquid environments with nanometer-scale resolution; allowing studies under liquid-phase conditions with external stimuli.	Could cause specimen damage; involves cumbersome operating conditions or sample preparation.	1) Reveals structural evolution of working catalysts. 2) Probes the evolution of atomistic crystallography.	[92, 93]
CLSM	Enables high-resolution, 3D imaging and real-time analysis of dynamic processes.	Low sensitivity; potential photobleaching; limited applicability for opaque or scattering samples.	Identifies 3D morphological environment of catalysts.	[68]
SECCM	A non-contact technique with no requirement for sample conductivity; maps out electrocatalytic activity on electrodes.	Hindered by slow scan rates; restricted to flat conductive surfaces	1) Identifies key intermediates. 2) Reveals the effect of a variety of reaction conditions.	[94]
DEMS	Real-time monitoring of electrochemical reactions with quantifications.	Necessitates specialized setup and skilled personnel; primarily detects gas-phase products.	Offers insights into reaction intermediates, products and pathways.	[95]

copper nanowires exhibited the same characteristic peak at 9005 eV as the copper reference material. The characteristic peak of Cu_2O was observed at 9013 eV. Consequently, the CuNNs remained metallic during the CO_2ER process (Fig. 5c).

To investigate transiently formed catalytically active surface species, structures of crucial intermediates, reaction pathways, and the impact of reaction conditions such as wettability at the electrolyte/electrode interface, *in-situ* IR technology is also a powerful tool. Due to the convective flow of the electrode surface in electrocatalytic CO_2ER, the attenuated total reflection (ATR) mode of operation is utilized to reduce interference from the electrolyte layer. Attenuated total reflectance surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) is an effective method for detecting adsorbed state species on the electrode surface, as it utilizes the evanescent infrared light waves at the bottom total reflection surface of an infrared window, such as Si [110] (Fig. 5d). Real-time observations of C_{1+} and C_{2+} routes of CO_2ER intermediates have been achieved using ATR-SEIRAS, notably following the synthesis of *CO (Fig. 5d) [109,110]. The reaction pathway and coverage/quantity of key surface species, which can be tracked by ATR-SEIRAS, are heavily associated with wettability characteristics under reaction conditions. ATR-SEIRAS was also employed to investigate the reaction intermediate of C-C couplings, a crucial step for the formation of C_{2+} products, where the formation of *OCCO via CO couplings was identified and excluded the involvement of *CHO [110]. The vital roles that cations and anions play in CO_2ER are also revealed by ATR-SEIRAS, altering our understanding of how CO_2 is transported to the catalyst surface. Moreover, ATR-SEIRAS provides a mechanistic framework for understanding the effect of wettability in CO_2ER by accurately identifying CO_2ER intermediates with and without wettability regulations.

The real-time quantification of localized CO_2 concentration at the electrolyte/electrode interface during electrocatalytic reactions can be achieved using *in-situ* fluorescence electrochemical measurements, which combine an electrochemical workstation with a fluorescence spectrophotometer (FEM, Fig. 5e). A probe molecule, such as 1-hydroxypyridine-3,6,8-trisulfonic acid (HPTS), exhibiting a distinctive fluorescence response to CO_2 molecules can be employed in FEM. The interfacial concentration of CO_2 molecules was effectively stabilized by the optimized three-phase catalytic system for infiltration, facilitating high catalytic selectivity at elevated current densities. Ultimately, the Cassie-Wenzel coexistence state is demonstrated to be the most advantageous wetting state for electrocatalytic CO_2ER to proceed. This method holds great promise for studying how the wettability of CO_2ER electrocatalysts can be regulated under practical working conditions, as it measures the CO_2 concentration at the catalyst interface and provides a theoretical framework for improved interfacial structure design and regulation.

4.2. Representative microscopies

Compared to the identification and quantification of surface reactive species and the chemical state of working electrocatalysts by spectroscopic techniques, microscopic methods enable the tracking of morphological properties and structural dynamics of working electrocatalysts, significantly enriching the toolkit for *in situ/operando* characterization of dynamically evolving liquid/solid interfaces. Microscopy allows for the observation of subtle changes in the catalyst during CO_2ER, as well as the local electrochemical activity and electron transfer processes occurring on the catalyst surface.

For instance, with the advancement of *in-situ* liquid-phase transmission electron microscopy (LP-TEM), it is now feasible to investigate physicochemical processes occurring in liquids with atomic-level resolution [111] (Fig. 6a). The use of LP-TEM, which combines an operating *in-situ* liquid cell and a TEM, is particularly advantageous in CO_2ER research because it enables direct monitoring of dynamic processes in the liquid phase with high spatial resolution [112]. In *in situ* LP-TEM, a

closed liquid cell that isolates a liquid phase of interest from the vacuum environment allows for the probing of working electrocatalysts under the application of external fields (heat, light, electrical, etc.). Although technical limitations still prevent the mass-application of LP-TEM in various scenarios, including an unavoidable compromise between the probing conditions and the practical condition of CO_2ER, an uneven distribution of the electric field, and potential specimen damage and radiolysis from the electron beam [92,93], the application of this powerful method in the study of liquid/solid interfaces has shown remarkable promise. The effect of wettability in CO_2ER can also be probed using LP-TEM for real-time visualization of the active sites and crystallographic atom topologies under working conditions.

Utilizing nanoparticle electrochemical cells to probe target entities with high spatial precision, scanning electrochemical cell microscope (SECCM) is a method for electrochemical visualization [113] (Fig. 6b). This technique enables the simultaneous study of local electrical behavior and physicochemical characteristics [94,114]. SECCM employs atomic force microscopy to precisely move and position the nanopipette probe in three dimensions with high accuracy. The distribution of H_2 bubble-shaped nuclei on the electrode surface can be studied by correlating the unique voltammetric peak currents with SECCM and a dual-channel probe [38]. When CO_2ER occurs at high reaction concentrations, this technique can be effectively used to investigate bubble nucleation and kinetics in wettability-modulated electrocatalysts. In order to enhance overall catalytic performance and efficiency, it is crucial to assist in the rational design of wettability structures for the next generation of high-performance catalysts for CO_2ER based on bubble nucleation and kinetics research.

The interfacial transport behavior of gaseous reactants/products and the interplay between catalytically active sites and ions in the electrolyte can both be significantly impacted by changes in wettability at the three-phase interface. Integrating microscopy and fluorescence techniques enables the examination of liquid-liquid and liquid-solid interfaces of the catalyst during CO_2ER and the study of how interfacial wettability affects the transportation of interfacial CO_2 transit and subsequent electrochemical reduction. Shi et al. [64] investigated the connection between the electrochemical performance and the wettability control structure of the TPC (three-phase coexistence) interface using a gas-phase connected H-cell with 1 M KOH. The three-phase interface on an Au/C electrode was imaged using confocal laser scanning microscopy (CLSM), revealing that the wettability of three catalysts, Au/C-F, Au/C-P-0.5, and Au/C-P-2.5, shifted from superhydrophobic to hydrophilic (Fig. 6c,d). The mass diffusion of redox species from the bulk solution to the vicinity of the active electrode surface is generally hampered, and the ohmic resistance at the electrode/electrolyte interface is increased as a result of increased bubble formation on the electrode surface during GERs. Analyzing bubble behavior in the context of distinct reaction pathways is crucial in CO_2ER. Burdyny et al. examined the gas release behavior during CO_2ER on three different electrocatalysts: nanoparticles, nanorods, and nanopins [68]. Compared to nanorods (31 μm) and nanoparticles (97 μm), the average separation width of bubbles on the nanoneedle surface was shorter (23 μm).

To investigate bubbles and identify the activity distribution on the catalyst surface, various microscopy techniques have been employed. Li et al. tracked the formation of nanobubbles on Pd-Ag nanoplates using differential interference contrast microscopy (DFM), observing numerous changes in the scattering intensity on different nanocatalysts. Furthermore, during the conversion of HCOOH to CO_2 and H_2 on Pd-Ag nanoplates, super-resolution microscopy (SRM) has been utilized to precisely locate the cores of individual nanobubbles at the nanoscale [116]. As a result, the local activity dispersion of nanocatalysts can be observed. To explore the relationship between catalyst wettability structure and activity, DFM and SRM techniques offer tremendous potential. The nucleation and release behavior of bubbles on the catalyst surface can be examined using a combination of microscopy and spectroscopy. Kim et al.'s proposed woodpile structured Ir catalyst was
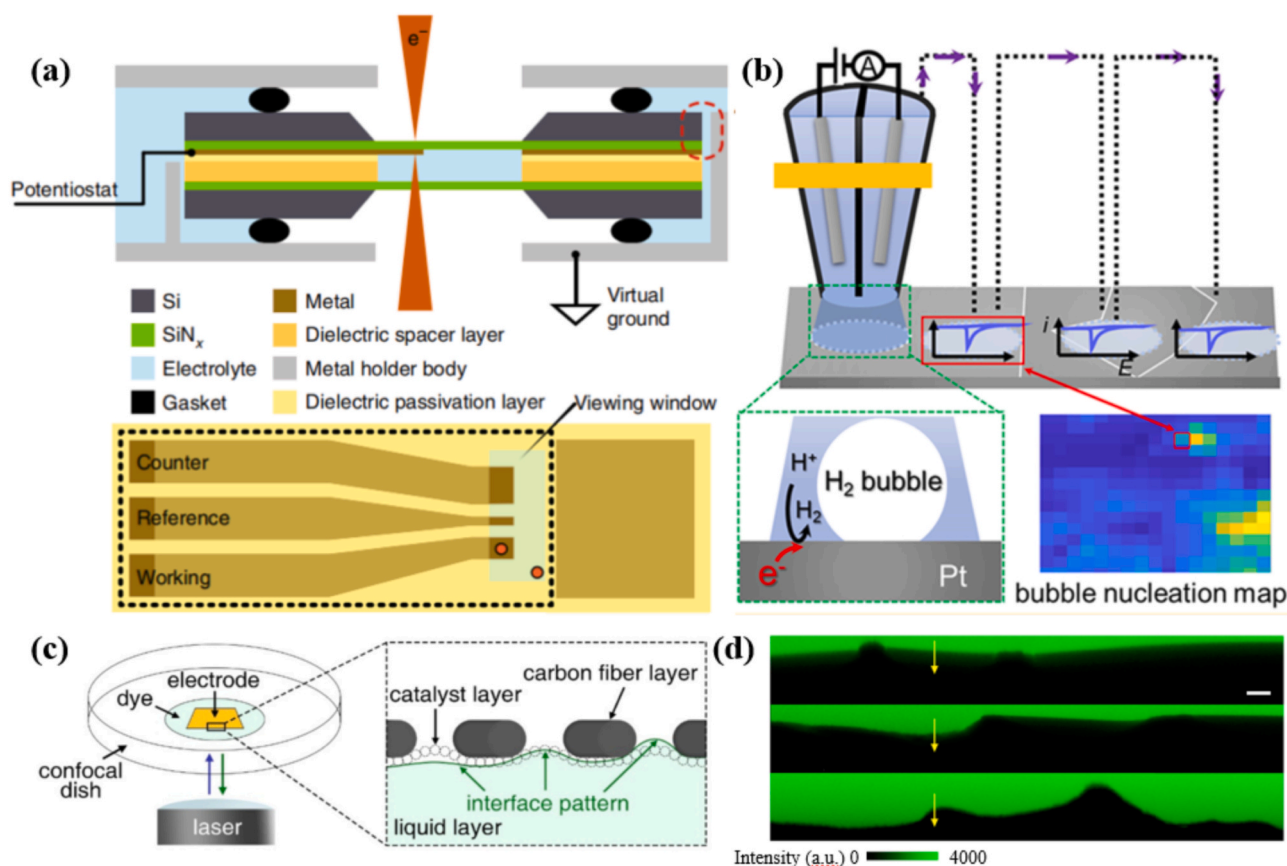
Fig. 6. Some microscopic techniques (a) an diagram of *in-situ* LP–TEM electrochemical cell design in cross-sectional; (b) Schematic diagram of the SECCM measurement for an H₂ bubble; (c) Schematic diagram of the method used to image the three-phase interface by confocal laser scanning microscopy; (d) Cross-sectional fluorescence images scanned. From top to bottom are Au/C-F, Au/C-P-0.5, and Au/C-P-2.5, respectively. Reproduced with permission from Ref. [115], Copyright © 2017 IOP ECS. Ref. [38], Copyright © 2019 American Chemical Society. Ref. [64], Copyright © 2020 Springer Nature.

evaluated using the fast Fourier transform (FFT) amplitude spectrum of scanning electron microscopy (SEM) and dynamic light scattering analysis spectra [117]. The high frequency of the FFT amplitude spectrum's peak indicates the rapid cycle of oxygen bubble formation and detachment. The dynamic light scattering analysis spectrum also reveals the distribution of O₂ bubble sizes. Consequently, this method holds great promise for comparing bubble behavior before and after altering the wettability of the electrocatalytic CO₂ER catalyst.

4.3. Other technologies

Differential electrochemical mass spectrometry (DEMS) has emerged as a robust tool bridging the gap between traditional half-cell studies and in-depth reaction analysis. This advanced technique combines the resilience of electrochemical half-cell experimentation with the high sensitivity and resolution of mass spectrometry, enabling real-time quantification of gaseous and volatile species involved in electrochemical reactions. Ye et al. [95] employed an online DEMS technique to investigate the effect of the local reaction environment on the electroreduction properties of CO₂. Moreover, a controlled study was conducted utilizing both DEMS and headspace chromatography methods to elucidate the mechanism of the reaction microenvironment in the vicinity of the electrode (Fig. 7a). This includes examining the influence of reactant transport limitation, cation-induced surface electric field interaction with intermediates, and oxide-derived electrode surface topography on facilitating the conversion process of CO₂ into CO. The application of DEMS to CO₂ER studies has opened new avenues for understanding the mechanistic pathways and surface interactions of this critical electrochemical reaction. The technique enables the

investigation of hydrophilic and hydrophobic surface interactions, which significantly influence mass transport and electrocatalytic activity, providing deeper insights into the underlying mechanisms of electrochemical reactions.

The use of ultrafast cameras [118] (Fig. 7b) or imaging technology has proven invaluable for understanding dynamic processes at hydrophobic interfaces in CO₂ER. Combining high temporal resolution and molecular-level observation capabilities, researchers can capture bubble formation, merging, and desorption in real-time. This enables the investigation of crucial processes, such as reactant diffusion, electrochemical nucleation, and the effects of surface roughness on the overall reaction. Insights gained from ultrafast imaging can aid in designing more efficient and effective electrocatalytic systems, advancing our understanding of CO₂ER and its potential for renewable energy production.

Several common continuous imaging techniques have been employed to study wettability-modulated bubble release behavior. According to Xu [61], nanostructured electrodes rapidly produced and released bubbles, which were only a tenth the size of those on flat, unmodulated surfaces. Additionally, widely used methods, such as contact angle and bubble adherence [10] (Fig. 7c), have been utilized to study the wettability behavior of electrode surfaces. These methods can be employed to study the surface of CO₂ER electrocatalysts and determine the effect of catalyst surface wettability modification on bubble nucleation and release behavior. Moreover, these methods can illustrate the connection between bubble attachment behavior and interfacial structure, essential knowledge for developing highly active and selective electrocatalysts.
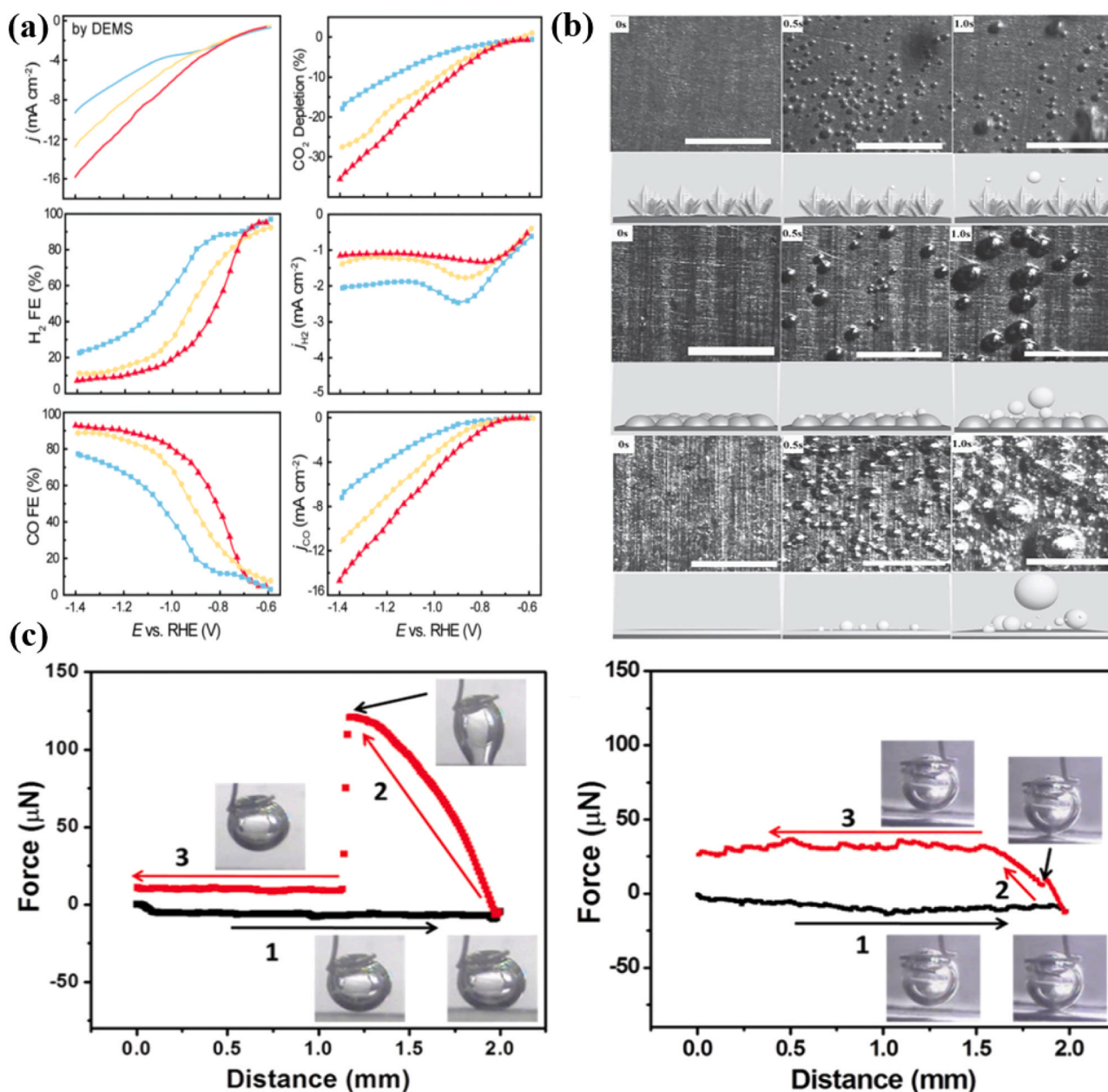
Fig. 7. Analysis of bubble and gas composition (a) Real-time DEMS results of CO$_2$ER over the same Ag/PTFE electrode as recorded during linear sweep voltammetry from 0.6 V to 1.4 V versus RHE at a scan rate of 1 mV s^{-1}; (b) Images of Pt nanoarray film, Pt nanosphere film, and Pt flat film of different gas bubbles generation behavior, scale: 500 μm; (c) Adhesive forces measurements of the gas bubbles on flat and nanostructured MoS$_2$ films. Reproduced with permission from Ref. [95], Copyright © 2020 Springer. Ref. [118], Copyright © 2015 Wiley-VCH. Ref. [61], Copyright © 2014 Wiley-VCH.

5. Effect of wettability and mechanisms at a molecular level

In electrode design, it is vital to not only engineer wettability but also comprehend the mechanism at a microscopic level. A mechanistic understanding of wettability's impact which has shown in Fig. 1 facilitates the improved design of hydrophobic/hydrophilic water interfaces to systematically regulate reaction pathways and kinetics. More specifically, the role of wettability in a multiphase catalytic process such as CO$_2$ER is crucial for controlling reaction pathways and kinetics, encompassing the transportation and diffusion of reactants [119], the adsorption/desorption of products, bubble kinetics, the thickness and species distribution in the EDL, and the regulation of reaction pathways and kinetics [7]. In essence, electrode surface wettability can dictate the intricacies and outcomes of CO$_2$ER, which will be expounded upon in the following sections.

5.1. Mass transport

The significance of mass transfer processes, which is not directly related to the intrinsic activity of catalytic materials, cannot be understated in electrocatalysis. Highly active catalysts are especially prone to mass transfer limitations, impeding the application of high-performance catalysts [120]. CO$_2$ER encompasses various mass transport processes, including CO$_2$ approaching the electrode surface, transportation of intermediate species within the heterogeneous electrocatalytic interface, and desorption of products from the catalytic center (i.e., the working electrode surface) into the bulk solution [63]. The transport of reactants (CO$_2$) and gaseous (CO, CH$_4$, C$_2$H$_4$, etc.) and liquid (CH$_3$OH, HCOOH, C$_2$H$_5$OH, etc.) products in the electrolyte solution frequently results in concentration polarization, impacting the thickness and distribution of the EDL. Consequently, mass transport plays a pivotal role in CO$_2$ER, as

the reaction rate surpasses the diffusion rate of kinetically relevant species [11,16].

5.1.1. Reactants

CO_2 and H_2O (generator of H*) are the two most important reactants in CO_2ER, with water-based electrolytes being both as a proton source and an ion-conductive medium [121]. The solubility of CO_2 in water is limited, leading to an imbalance between reaction and diffusion rates [122]. Under alkaline conditions, CO_2 diffusion lengths can be as low as tens of nanometers [73], and the pH-dependent CO_2 concentration exhibits significant undersaturation even at low current densities of 10 mA/cm^2 [11], thereby favoring HER and reducing catalyst productivity due to mass transport limitations [79]. Researchers have tackled this challenge by modifying the electrode surface to be hydrophobic (aerophilic), consequently increasing the thickness of the EDL and enhancing CO_2 transport rates while limiting H_2O transport. Recently, there has been increasing interest in designing GDEs as an effective approach to mitigate CO_2 concentration limitations by controlling mass transport (Fig. 8) [123]. GDEs enable CO_2 to diffuse only short distances to reach the electroactive sites on the catalyst surface, thereby alleviating mass transportation limitations. However, to expedite CO_2 transport, GDEs must be aerophilic, which may influence the reactant transport process. Nevertheless, it has been demonstrated that proper design and optimization can ensure the reactant transport process is no longer a constraint in CO_2ER when employing GDEs.

5.1.2. Products

Wettability plays a crucial role in bubble adhesion to the catalyst or a working electrode, regulating product diffusion and transport [124]. Bubbles form during CO_2ER and nucleate on the surface of electrocatalysts, growing in size and eventually released. In addition to macroscopic bubbles, studies have confirmed the presence of nanoscale bubbles [125]. Bubble accumulation at electrochemically active sites negatively impacts electrocatalytic performance. In industrial settings with high current densities, intense product bubble evolution can lead to reduced activity and even structural damage to the catalyst [119]. Liquid and side products can also affect the liquid environment, altering local instantaneous pH and ion concentration. Salt and foreign ion deposition at the gas-liquid interface often leads to electrode lifetime reduction, particularly in GDEs [41]. Furthermore, intermediate products near the electrode can serve as reactants for further reduction. Therefore, effective mass transport management can be an efficient way to adjust end product partitioning and working electrode lifetime. For instance, if CO cannot be removed promptly, it is more likely that CO will participate in C-C bond coupling by increasing local CO coverage [126].

While various methods to modulate mass transport exist, such as forced convection techniques (e.g., magnetic stirring, flow electrolytic cells, rotating electrodes), environmental magnetic fields [127], thin electrolytic cells [128], and ultramicroelectrodes [129], these methods have limitations and are challenging to apply to specific products. Alternatively, modifying the catalyst surface wettability can improve performance by regulating mass transport, resulting in advantages like designing specific C_{2+} products with enhanced catalyst stability.

5.2. Reaction pathway and kinetics

Modifying mass transport affects the diffusion of reactants, products, transient surface species, and ultimately modulates reaction pathways and kinetics. It has been emphasized that theoretical results can be obtained by measuring data in the absence of mass transport effects [120]. While wettability does not directly control reaction pathways and kinetics, understanding these aspects is crucial in elucidating the mechanism at a molecular level.

The initiation of CO_2ER requires the adsorption and activation of inert CO_2 molecules onto the cathode surface [130]. Surface wettability can strongly influence the adsorption and desorption equilibrium, governing the coverage of intermediates such as CO_2, COOH, and CO. For instance, hydrophobic (aerophilic) surfaces promote CO_2 adsorption and liquid species desorption (H_2O, C_2H_4, CH_3OH, $HCOO^-$, etc.), resulting in higher CO coverage and lower coverage of HER and liquid product intermediates, including H, HCO, HCCO, and HCOO on the cathode surface. Conversely, hydrophilic (aerophobic) surfaces decrease CO_2 adsorption while increasing gas product desorption (H_2, CO, CH_4, etc.), leading to lower coverage of gas product intermediates such as H*, CO*, and *CH_3. These surface modifications can significantly affect CO_2ER selectivity and efficiency, making surface wettability an essential factor for modulating electrocatalytic performance [131].

In addition to intrinsic electronic interactions between adsorbates and electrocatalyst surfaces, the binding energies of kinetically relevant surface species on a working electrode generally depend on adsorbate coverage, significantly impacting reaction pathways and rates under relevant conditions [132]. For instance, a low coverage of *CO can result in a high binding energy of *CO species, while high coverage can weaken the binding energy because of the lateral dipole interactions between neighboring CO molecules and the binding of CO* onto less coordinated surface science, e.g., atop site [133–135]. The relationship between binding energy and coverage has essential implications for carbon-carbon coupling probability, as carbon surface coverage must be sufficiently high for substantial reaction rates. Notably, the coverage of kinetically relevant species is strongly associated with mass transport and wettability properties at the electrode/electrolyte interface. Therefore, screening potential catalyst materials without properly incorporating adsorbate interactions can be misleading [141]. As a result, the coverage and adsorption binding energy of *CO on a working electrode can ultimately govern reaction pathways and product distribution, which can ideally be engineered via surface wetting property modulation. Surface adsorbate stability, interactions between reaction intermediates (e.g., C-C coupling reactions) [136], and applied bias concerning individual electron and proton reaction onset potentials
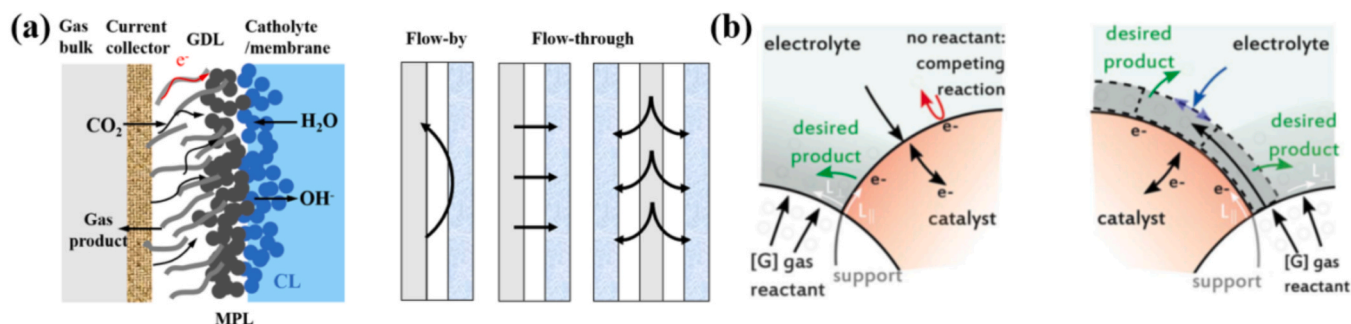
Fig. 8. (a) Different diffusion processes in GDE; (b) Effect of wettability modification on diffusion process in GDE. Reproduced with permission from Ref. [72], Copyright © 2020 The American Association for the Advancement of Science.

dictate CO$_2$ER reaction pathways and product selectivities (Fig. 9b illustrates the case of C1 products) [137–139]. Consequently, interaction and binding energy of reaction intermediates to the catalyst surface can lead to different pathways and chemical products, significantly affecting catalytic activity and selectivity [140].

5.3. Mechanism to applications

Despite the identification of numerous promising catalysts for CO$_2$ER, significant obstacles hinder their industrial applications, including catalyst stability, energy efficiency, and controllability over catalytic selectivity [142]. One important handle in addressing these challenges is to modify the wettability of the catalyst surface, which can alter the mass transfer process and lead to different product yields. This approach provides valuable insights for improving catalyst performance and better utilizing wettability modification in CO$_2$ER catalyst design [65,137]. Developing active, selective, and stable catalysts is crucial for industrial progress, requiring the identification of specific structure-reaction relationships to guide catalyst design.

In a recent study [65], researchers investigated the relationship between hydrophilicity and productivity of formic acid and carbon monoxide at a fixed voltage (-0.7 V vs RHE) using various polymeric and molecular modifiers to alter copper surface wettability. The results demonstrated that partial wettability could be achieved through chemical methods, and a correlation between wettability and products existed. However, chemical methods may face issues with stability, impurities, oxidation, and active site coverage, making it challenging to tune the full spectrum of wettability. To overcome these limitations, new wettability modification methods should be developed, such as creating processed surface micro-nano structures, supplemented by secondary tuning using chemical methods. This strategy can help achieve the desired wettability regulation and obtain active, selective, and stable catalysts. For instance, spatially, temporally, and frequency-modulated ultra-fast lasers can modify copper surface micro and nanostructures by controlling processing parameters. By combining a single chemical modifier with micro-nano structure modification can potentially achieve a full spectrum of wettability while avoiding the drawbacks of sole chemical methods. From fundamental perspective, the structure-reaction relationship is crucial for developing new selective CO$_2$ER electrocatalysts and can be probed by various *in-situ/operando* means as listed in Section 4. The progress of wettability control in electrocatalytic CO$_2$ reduction with representative studies highlighted is shown in Fig. 10, although this field is developing quickly, research on the relationships of structure-wettability-selectivity/activity is still lacking. Combining multiple wettability modification methods and multiple microscopic characteristics for mechanism studies offers a viable path toward understanding reliable structure-wettability-selectivity/activity relationships that can guide the efficient design of industrial catalysts.

6. Summary and outlook

In this review, we review the fundamentals of wetting mechanism and the ideal wetting mechanism under an electric field in CO$_2$ER. Typical approaches for regulating wettability, including surface coating, micro-nano structures, and surface chemical modification are summarized and representative techniques, including ultra-fast laser direct writing, thin film deposition, nanoimprint lithography and 4D printing are introduced and reviewed. Advanced in-situ/*operando* spectroscopic, microscopic, and other catalyst characterization techniques, specifically suitable for analyzing liquid/solid interfaces under dynamically evolving conditions, are introduced and analyzed in association with their potential applications in the characterization/manipulation of wettability and electrocatalysis. Finally, we summarize the correlations between wettability and the outcome of electrocatalytic CO$_2$ER in terms of reaction pathways and kinetics at a molecular level, outlining the strategy to design efficient CO$_2$ER electrocatalysts with high selectivity, high reaction rate, minimal overpotential, and good stability via wettability modulation.

While the manipulation of wettability has been investigated by various established means, the development of advanced methodologies is critical and imperative for a variety of practical reasons. For example, surface coatings risk concealing catalyst active sites, and distinct chemical properties might hinder the generation of micro-nano structures; since most techniques alter both the chemical characteristics and surfacer micro/nano structures, wettability is no longer a single variable and renders the elucidation of the working mechanism from a fundamental perspective challenging; the stability of a hydrophilic or hydrophobic surface fabricated by existing methods still requires improvement since the catalyst surface often suffers from gradually loss of its hydrophilicity/hydrophobicity during electrochemical reactions and more efficient, accurate and advanced techniques are needed. Consequently, exploring advanced wettability manipulation techniques, such as nanoimprint lithography, ultrafast laser direct writing, and 4D printing, is essential, since the state-of-the-art technologies facilitate modulation at atomic, nanoscale, and micron levels, broadening CO$_2$ electrocatalysis applications through multi-scale hydrophilic modulation. Accurate control of catalyst surface hydrophobicity enables targeted regulation of reaction rates, pathways, and product distribution, ultimately enhancing electrocatalytic efficiency and selectivity.

A comprehensive understanding of CO$_2$ER mechanisms is vital for devising highly active and selective catalysts; however, existing knowledge remains vague and contested because of a lack of proper in-situ/*operando* tools to explore a dynamically evolving electrode/electrolyte interface. Advanced detection and characterization methodologies, such as CLSM, LP-TEM, infrared spectroscopy, XAS and APXPS, are essential tools for examining the dynamic shifts in interfacial wettability during reactions, including active sites, reaction pathways, and selectivity in the CO$_2$ER process, where sufficient temporal resolution to
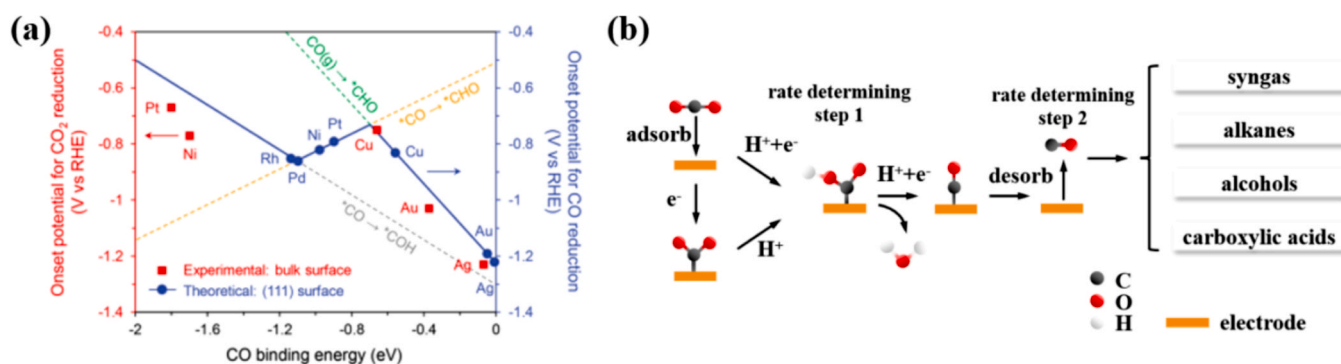

Fig. 9. (a) Comparison of the activity of selected transition metal catalysts, (b) Possible reaction pathways for the electrocatalytic reduction. Reproduced with permission from Ref. [141], Copyright © 2017 American Chemical Society.
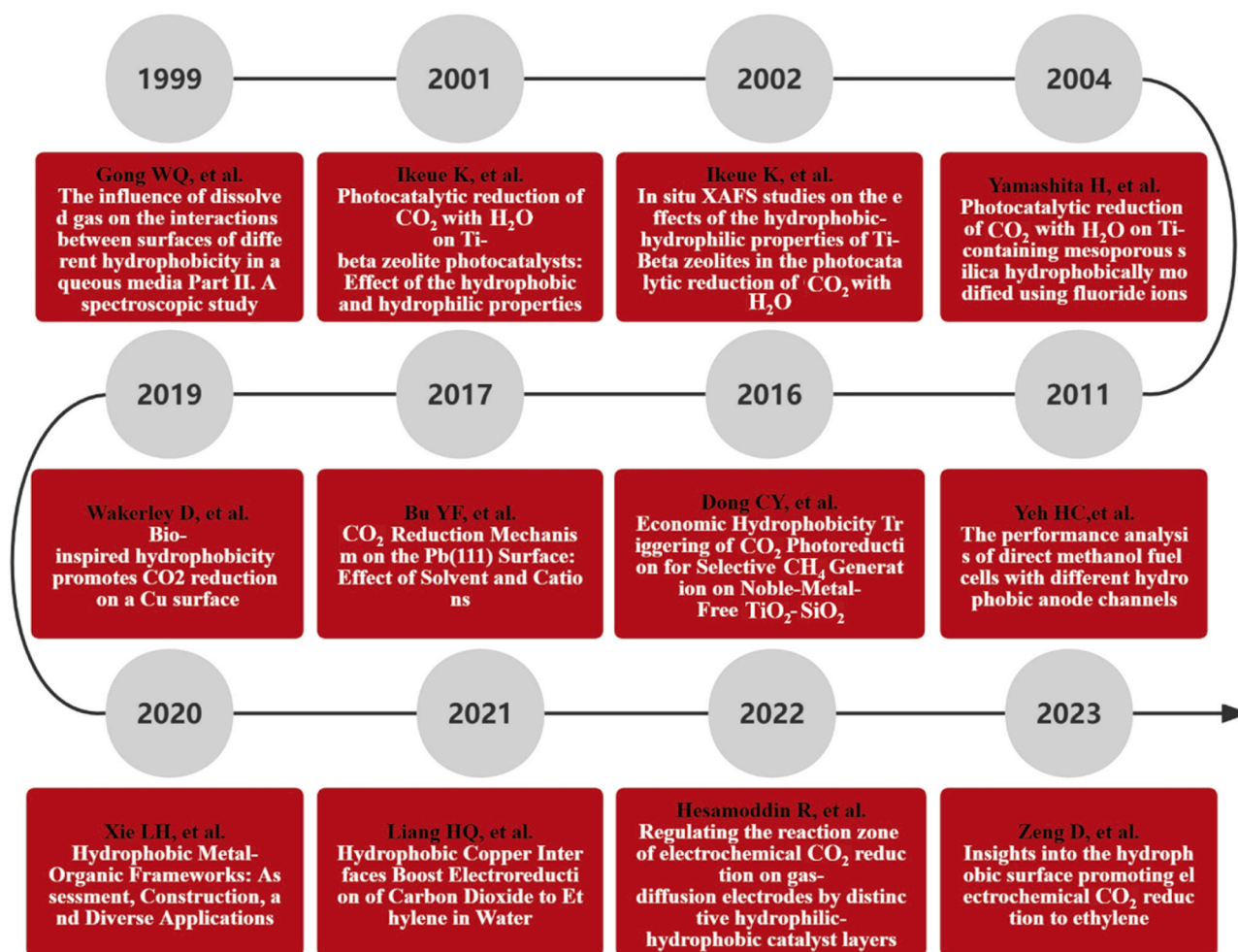
Fig. 10. The progress of wettability control in electrocatalytic CO₂ reduction [35,71,143–153].

monitor rapid changes in catalyst morphology and oxidation state, while simultaneously accounting for the effects of local electrolyte condition instability on measurement time scales.

For industrial-scale applications operating at high current densities, harnessing the benefits of wettability manipulation—such as reduced overpotential, improved selectivity, and enhanced stability—is crucial. For example, designing a hydrophobic surface can mitigate flooding and clogging challenges in GDLs. Future research should concentrate on devising wettability manipulation strategies and catalyst designs appropriate for industrial-scale applications that fulfill practical demands.

Multiscale computational modeling serves as a powerful tool for unveiling the impact of wettability on CO₂ER. Future research should develop multiscale computational approaches that integrate the effects on reaction pathways and kinetics. Additionally, kinetic models can be employed to investigate wettability-regulated transport and diffusion processes of reactants, adsorption/desorption of products, bubble kinetics, thickness, and material distribution in the EDL, as well as regulation of reaction pathways and kinetics. Ultimately, these insights into the modulation mechanism between wettability and CO₂ER will facilitate more effective catalyst surface design.

Wettability control not only plays an important role in the complex catalytic processes at the electrolyte/electrode interface under CO₂ER, but also can be extended to OER, ORR, HER, etc. For the gas precipitation reaction GERs (OER and HER), designing hydrophilic/hydrophobic catalyst surfaces will facilitate bubble separation, avoid bubble

aggregation that reduces the availability of exposed active sites, and impede mass transfer in the liquid phase, thus slowing down charge transfer and leading to a decrease in electrocatalytic activity and stability. However, designing hydrophobic/gasophilic catalyst surfaces is more favorable for gas-consumption reaction GCR (ORR and NRR), which will allow an unobstructed gas diffusion path to continuously supply sufficient gas reactants to the catalytic sites and will form abundant gas/electrolyte/catalyst three-phase contact lines. In addition, wettability has different effects on the mass transfer process in different types of reactions. Changes in the mass transfer process can cause changes in the binding energy of intermediates, which can affect the reactivity. In addition, when there are multiple products, many intermediates compete with each other so that the change in binding energy affects the reaction pathway.In conclusion, advancing the regulation of wettability in electrocatalysis for large-scale industrial applications necessitates a deeper understanding of the underlying mechanisms through the use of sophisticated detection and characterization techniques. This approach will enable the rational design of catalysts with tailored wettability, ultimately enhancing electrocatalytic efficiency, selectivity, and limiting current density by elucidating the connection between wettability regulation and catalytic performance. Consequently, future research should concentrate on exploring the interplay between catalyst wettability and electrocatalytic performance while leveraging advanced characterization methods to engineer catalysts with superior wettability control.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

Acknowledgements

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2023.123293.

References

[1] J.A. Rabinowitz, M.W. Kanan, The future of low-temperature carbon dioxide electrolysis depends on solving one basic problem, Nat. Commun. 11 (2020) 5231.

[2] Y. Sun, Z. Lin, S.H. Peng, V. Sage, Z. Sun, A critical perspective on CO_2 conversions into chemicals and fuels, J. Nanosci. Nanotechnol. 19 (2019) 3097–3109.

[3] M.A. Quader, S. Ahmed, R.A.R. Ghazilla, S. Ahmed, M. Dahari, A comprehensive review on energy efficient CO_2 breakthrough technologies for sustainable green iron and steel manufacturing, Renew. Sust. Energ. Rev. 50 (2015) 594–614.

[4] D. Gao, Y. Zhang, Z. Zhou, F. Cai, X. Zhao, W. Huang, Y. Li, J. Zhu, P. Liu, F. Yang, G. Wang, X. Bao, Enhancing CO_2 electroreduction with the metal-oxide interface, J. Am. Chem. Soc. 139 (2017) 5652–5655.

[5] H.S. Jeon, S. Kunze, F. Scholten, B. Roldan Cuenya, Prism-shaped Cu nanocatalysts for electrochemical CO_2 reduction to ethylene, ACS Catal. 8 (2017) 531–535.

[6] Y.-B. Chang, C. Zhang, X.-L. Lu, W. Zhang, T.-B. Lu, Graphdiyne enables ultrafine Cu nanoparticles to selectively reduce CO_2 to C_{2+} products, Nano Res. 15 (2021) 195–201.

[7] Z. Cai, Y. Zhang, Y. Zhao, Y. Wu, W. Xu, X. Wen, Y. Zhong, Y. Zhang, W. Liu, H. Wang, Y. Kuang, X. Sun, Selectivity regulation of CO_2 electroreduction through contact interface engineering on superwetting Cu nanoarray electrodes, Nano Res. 12 (2018) 345–349.

[8] X. Zhang, Y. Zhang, F. Li, C.D. Easton, A.M. Bond, J. Zhang, Ultra-small Cu nanoparticles embedded in N-doped carbon arrays for electrocatalytic CO_2 reduction reaction in dimethylformamide, Nano Res. 11 (2018) 3678–3690.

[9] J. Chen, T. Wang, Z. Li, B. Yang, Q. Zhang, L. Lei, P. Feng, Y. Hou, Recent progress and perspective of electrochemical CO_2 reduction towards C_2-C_5 products over non-precious metal heterogeneous electrocatalysts, Nano Res. 14 (2021) 3188–3207.

[10] W. Xu, Z. Lu, X. Sun, L. Jiang, X. Duan, Superwetting electrodes for gas-involving electrocatalysis, Acc. Chem. Res. 51 (2018) 1590–1598.

[11] P. Lobaccaro, M.R. Singh, E.L. Clark, Y. Kwon, A.T. Bell, J.W. Ager, Effects of temperature and gas-liquid mass transfer on the operation of small electrochemical cells for the quantitative evaluation of CO_2 reduction electrocatalysts, Phys. Chem. Chem. Phys. 18 (2016) 26777–26785.

[12] D. Wu, J. Zhang, M.-J. Cheng, Q. Lu, H. Zhang, Machine learning investigation of supplementary adsorbate influence on Copper for enhanced electrochemical CO_2 reduction performance, J. Phys. Chem. C 125 (2021) 15363–15372.

[13] K. Liu, X. Yao, L. Jiang, Recent developments in bio-inspired special wettability, Chem. Soc. Rev. 39 (2010) 3240–3255.

[14] T. Li, J. Wang, F. Wang, L. Zhang, Y. Jiang, H. Arandiyan, H. Li, The effect of surface wettability and coalescence dynamics in catalytic performance and catalyst preparation: a review, ChemCatChem 11 (2019) 1576–1586.

[15] C. Huang, Z. Guo, The wettability of gas bubbles: from macro behavior to nano structures to applications, Nanoscale 10 (2018) 19659–19672.

[16] A. Angulo, P. van der Linde, H. Gardeniers, M. Modestino, D. Fernández Rivas, Influence of bubbles on the energy conversion efficiency of electrochemical reactors, Joule 4 (2020) 555–579.

[17] J.X. Feng, H. Xu, S.H. Ye, G. Ouyang, Y.X. Tong, G.R. Li, Silica-polypyrrole hybrids as highperformance metal-freeelectrocatalysts for the hydrogen evolution reaction in neutral media, Angew. Chem. Int. Ed. Engl. 56 (2017) 8120–8124.

[18] R. Shi, L. Shang, T. Zhang, Three phase interface engineering for advanced catalytic applications, ACS Appl. Energy Mater. 4 (2021) 1045–1052.

[19] Z.Z. Niu, F.Y. Gao, X.L. Zhang, P.P. Yang, R. Liu, L.P. Chi, Z.Z. Wu, S. Qin, X. Yu, M.R. Gao, Hierarchical Copper with inherent hydrophobicity mitigates electrode

[20] J. Wicks, M.L. Jue, V.A. Beck, J.S. Oakdale, N.A. Dudukovic, A.L. Clemens, S. Liang, M.E. Ellis, G. Lee, S.E. Baker, E.B. Duoss, E.H. Sargent, 3D-printable fluoropolymer gas diffusion layers for CO_2 electroreduction, Adv. Mater. 33 (2021), e2003855.

[21] N. Li, W. Zhao, F. Li, L. Liu, Y. Liu, J. Leng, A 4D-printed programmable soft network with fractal design and adjustable hydrophobic performance, Matter (3) (2023) 940–962.

[22] H. Zhang, G. Zhao, S. Wu, Y. Alsaid, W. Zhao, X. Yan, L. Liu, G. Zou, J. Lv, X. He, Z. He, J. Wang, Solar anti-icing surface with enhanced condensate self-removing at extreme environmental conditions, Proc. Natl. Acad. Sci. U. S. A. 118 (2021), e2100978118.

[23] C. Zhang, Z. Xu, N. Han, Y. Tian, T. Kallio, C. Yu, L. Jiang, Superaerophilic/superaerophobic cooperative electrode for efficient hydrogen evolution reaction via enhanced mass transfer, Sci. Adv. 9 (2023) 1–10.

[24] D. Wang, Q. Sun, M.J. Hokkanen, C. Zhang, F.Y. Lin, Q. Liu, S.P. Zhu, T. Zhou, Q. Chang, B. He, Q. Zhou, L. Chen, Z. Wang, R.H.A. Ras, X. Deng, Design of robust superhydrophobic surfaces, Nature 582 (2020) 55–59.

[25] S. Dong, C. Zhang, Z. Yue, F. Zhang, H. Zhao, Q. Cheng, G. Wang, J. Xu, C. Chen, Z. Zou, Z. Dou, H. Yang, Overall design of anode with gradient ordered structure with low iridium loading for proton exchange membrane water electrolysis, Nano. Lett. 22 (2022) 9434–9440.

[26] J.L. Yong, F. Chen, Q. Yang, Z.D. Jiang, X. Hou, A review of femtosecond-laser-induced underwater superoleophobic surfaces, Adv. Mater. Interfaces 5 (2018) 1701370.

[27] Z. Li, X. Wei, Z. Yang, Pulsed laser 3D-micro/nanostructuring of materials for electrochemical energy storage and conversion, Prog. Mater. Sci. 133 (2023), 101052.

[28] J. Yong, Q. Yang, X. Hou, F. Chen, Nature-Inspired superwettability achieved by femtosecond lasers, Ultra Sci. 2022 (2022) 1–51.

[29] F. Xia, L. Jiang, Bio-Inspired, Smart, Multiscale interfacial materials, Adv. Mater. 20 (2008) 2842–2858.

[30] H. Liu, Z. Li, J. Hu, Z. Qiu, W. Liu, J. Lu, J. Yin, Self-supported cobalt oxide electrocatalysts with hierarchical chestnut burr-like nanostructure for efficient overall water splitting, Chem. Eng. J. 435 (2022) 134995.

[31] C. Li, L. Jiang, J. Hu, C. Xu, Z. Li, W. Liu, X. Zhao, B. Zhao, Superhydrophilic-superhydrophobic multifunctional janus foam fabrication using a spatially shaped femtosecond laser for fog collection and detection, Acs. Appl. Mater. Interfaces 14 (2022) 9873–9881.

[32] S. Zhang, L. Xu, J. Wu, Y. Yang, C. Zhang, H. Tao, J. Lin, L. Huang, W. Fang, K. Shi, X. Dong, Femtosecond laser micro-nano processing for boosting bubble releasing of gas evolution reactions, Nano Res. 15 (2021) 1672–1679.

[33] P. Wang, T. Hayashi, Q. Meng, Q. Wang, H. Liu, K. Hashimoto, L. Jiang, Highly boosted oxygen reduction reaction activity by tuning the underwater wetting state of the superhydrophobic electrode, Small 13 (2017) 1601250.

[34] H. Matsui, N. Ishiguro, T. Uruga, O. Sekizawa, K. Higashi, N. Maejima, M. Tada, Operando 3D visualization of migration and degradation of a platinum cathode catalyst in a polymer electrolyte fuel cell, Angew. Chem. Int. Ed. Engl. 56 (2017) 9371–9375.

[35] H.-Q. Liang, S. Zhao, X.-M. Hu, M. Ceccato, T. Skrydstrup, K. Daasbjerg, Hydrophobic Copper interfaces boost electroreduction of carbon dioxide to ethylene in water, ACS Catal. 11 (2021) 958–966.

[36] P. An, L. Wei, H. Li, B. Yang, K. Liu, J. Fu, H. Li, H. Liu, J. Hu, Y.-R. Lu, H. Pan, T.-S. Chan, N. Zhang, M. Liu, Enhancing CO_2 reduction by suppressing hydrogen evolution with polytetrafluoroethylene protected copper nanoneedles, J. Mater. Chem. A 8 (2020) 15936–15941.

[37] L. Xiong, X. Fu, Y. Zhou, P. Nian, Z. Wang, Q. Yue, Precise site-hydrophobicity modulation for boosting high-performance CO_2 electroreduction, ACS Catal. 13 (2023) 6652–6660.

[38] Y. Wang, E. Gordon, H. Ren, Mapping the nucleation of H_2 bubbles on polycrystalline Pt via scanning electrochemical cell microscopy, J. Phys. Chem. Lett. 10 (2019) 3887–3892.

[39] H. Pang, X. Meng, P. Li, K. Chang, W. Zhou, X. Wang, X. Zhang, W. Jevasuwan, N. Fukata, D. Wang, J. Ye, Cation vacancy-initiated CO_2 photoreduction over ZnS for efficient formate production, ACS Energy Lett. 4 (2019) 1387–1393.

[40] A. Shavorskiy, X. Ye, O. Karslioglu, A.D. Poletayev, M. Hartl, I. Zegkinoglou, L. Trotochaud, S. Nemsak, C.M. Schneider, E.J. Crumlin, S. Axnanda, Z. Liu, P. N. Ross, W. Chueh, H. Bluhm, Direct mapping of band positions in doped and undoped hematite during photoelectrochemical water splitting, J. Phys. Chem. Lett. 8 (2017) 5579–5586.

[41] M. Li, M.N. Idros, Y. Wu, T. Burdyny, S. Garg, X.S. Zhao, G. Wang, T.E. Rufford, The role of electrode wettability in electrochemical reduction of carbon dioxide, J. Mater. Chem. A 9 (2021) 19369–19409.

[42] Y. Liang, Y. Han, J.-s Li, J. Wang, D. Liu, Q. Fan, Wettability control in electrocatalyst: a mini review, J. Energy Chem. 70 (2022) 643–655.

[43] L. Zhao, F. Ran, Electrolyte-philicity of electrode materials, Chem. Commun. 59 (2023) 6969–6986.

[44] L. Zhao, Y. Li, M. Yu, Y. Peng, F. Ran, Electrolyte-wettability issues and challenges of electrode materials in electrochemical energy storage, energy conversion, and beyond, Adv. Sci. 10 (2023), e2300283.

[45] A.W. Adamson, A.P. Gast, Physical chemistry of surfaces, Interscience Publishers, New York, 1967.

[46] C.M. Gabardo, C.P. O'Brien, J.P. Edwards, C. McCallum, Y. Xu, C.-T. Dinh, J. Li, E.H. Sargent, D. Sinton, Continuous carbon dioxide electroreduction to

concentrated multi-carbon products using a membrane electrode assembly, Joule 3 (2019) 2777–2791.

[47] D. Bonn, J. Eggers, J. Indekeu, J. Meunier, E. Rolley, Wetting and spreading, Rev. Mod. Phys. 81 (2009) 739–805.

[48] Z. Lu, Y. Li, X. Lei, J. Liu, X. Sun, Nanoarray based "superaerophobic" surfaces for gas evolution reaction electrodes, Mater. Horiz. 2 (2015) 294–298.

[49] Keith Scott, Justo Lobato, Determination of a mass-transfer coefficient using the limiting-current technique, Chem. Educ. 7 (2002) 214–219.

[50] D. Bohra, J.H. Chaudhry, T. Burdyny, E.A. Pidko, W.A. Smith, Modeling the electrical double layer to understand the reaction environment in a CO2 electrocatalytic system, Energy Environ. Sci. 12 (2019) 3380–3389.

[51] E.W. Lees, B.A.W. Mowbray, F.G.L. Parlane, C.P. Berlinguette, Gas diffusion electrodes and membranes for CO2 reduction electrolysers, Nat. Rev. Mater. 7 (2021) 55–64.

[52] M.E. Leonard, L.E. Clarke, A. Forner-Cuenca, S.M. Brown, F.R. Brushett, Investigating electrode flooding in a flowing electrolyte, Gas. -Fed. Carbon Dioxide Electro, ChemSusChem 13 (2020) 400–411.

[53] E.R. Cofell, U.O. Nwabara, S.S. Bhargava, D.E. Henckel, P.J.A. Kenis, Investigation of electrolyte-dependent carbonate formation on gas diffusion electrodes for CO2 electrolysis, ACS Appl. Mater. Interfaces 13 (2021) 15132–15142.

[54] K. Yang, R. Kas, W.A. Smith, T. Burdyny, Role of the carbon-based gas diffusion layer on flooding in a gas diffusion electrode cell for electrochemical CO2 reduction, ACS Energy Lett. 6 (2020) 33–40.

[55] T. Wu, G. Wang, F. Zhan, Q. Dong, Q. Ren, J. Wang, J. Qiu, Surface-treated carbon electrodes with modified potential of zero charge for capacitive deionization, Water Res 93 (2016) 30–37.

[56] D. Ma, Y. Wang, X. Han, S. Xu, J. Wang, Electrode configuration optimization of capacitive deionization cells based on zero charge potential of the electrodes, Sep. Purif. Technol. 189 (2017) 467–474.

[57] S. Ringe, E.L. Clark, J. Resasco, A. Walton, B. Seger, A.T. Bell, K. Chan, Understanding cation effects in electrochemical CO2 reduction, Energy Environ. Sci. 12 (2019) 3001–3014.

[58] S. Ringe, C.G. Morales-Guio, L.D. Chen, M. Fields, T.F. Jaramillo, C. Hahn, K. Chan, Double layer charging driven carbon dioxide adsorption limits the rate of electrochemical carbon dioxide reduction on Gold, Nat. Commun. 11 (2020) 33.

[59] Thomas B. Jones, On the relationship of dielectrophoresis and electrowetting, Langmuir 18 (11) (2002) 4437–4443.

[60] J.J. Zhang, L.B. Lv, T.J. Zhao, Y.X. Lin, Q.Y. Yu, J. Su, S.I. Hirano, X.H. Li, J. S. Chen, Engineering the interfaces of superadsorbing graphene-based electrodes with gas and electrolyte to boost gas evolution and activation reactions, ChemSusChem 11 (2018) 2306–2309.

[61] Z. Lu, W. Zhu, X. Yu, H. Zhang, Y. Li, X. Sun, X. Wang, H. Wang, J. Wang, J. Luo, X. Lei, L. Jiang, Ultrahigh hydrogen evolution performance of under-water "superaerophobic" MoS2 nanostructured electrodes, Adv. Mater. 26 (2014) 2683–2687, 2615.

[62] Q. Zhang, M. Zhou, G. Ren, Y. Li, Y. Li, X. Du, Highly efficient electrosynthesis of hydrogen peroxide on a superhydrophobic three-phase interface by natural air diffusion, Nat. Commun. 11 (2020) 1731.

[63] F. Pan, Y. Yang, Designing CO2 reduction electrode materials by morphology and interface engineering, Energy Environ. l Sci. 13 (2020) 2275–2309.

[64] R. Shi, J. Guo, X. Zhang, G.I.N. Waterhouse, Z. Han, Y. Zhao, L. Shang, C. Zhou, L. Jiang, T. Zhang, Efficient wettability-controlled electroreduction of CO2 to CO at Au/C interfaces, Nat. Commun. 11 (2020) 3028.

[65] A.K. Buckley, M. Lee, T. Cheng, R.V. Kazantsev, D.M. Larson, W.A. Goddard, III, F.D. Toste, F.M. Toma, Electrocatalysis at organic-metal interfaces: Identification of structure-reactivity relationships for CO2 reduction at modified Cu surfaces, J. Am. Chem. Soc. 141 (2019) 7355–7364.

[66] G. Ma, O.A. Syzgantseva, Y. Huang, D. Stoian, J. Zhang, S. Yang, W. Luo, M. Jiang, S. Li, C. Chen, M.A. Syzgantseva, S. Yan, N. Chen, L. Peng, J. Li, B. Han, A hydrophobic Cu/Cu2O sheet catalyst for selective electroreduction of CO to ethanol, Nat. Commun. 14 (2023) 501.

[67] Y. Lin, T. Wang, L. Zhang, G. Zhang, L. Li, Q. Chang, Z. Pang, H. Gao, K. Huang, P. Zhang, Z.-J. Zhao, C. Pei, J. Gong, Tunable CO2 electroreduction to ethanol and ethylene with controllable interfacial wettability, Nat. Commun. 14 (2023) 3575.

[68] T. Burdyny, P.J. Graham, Y. Pang, C.-T. Dinh, M. Liu, E.H. Sargent, D. Sinton, Nanomorphology-enhanced gas-evolution intensifies CO2 reduction electrochemistry, ACS Sustain. Chem. Eng. 5 (2017) 4031–4040.

[69] K. Li, S. Zou, J. Zhang, Y. Huang, L. He, X. Feng, Superhydrophobicity-enabled efficient electrocatalytic CO2 reduction at a high temperature, ACS Catal. 13 (2023) 9346–9351.

[70] M. Fang, M. Wang, Z. Wang, Z. Zhang, H. Zhou, L. Dai, Y. Zhu, L. Jiang, Hydrophobic, Ultrastable Cu8+ for robust CO2 electroreduction to C2 products at ampere-current levels, J. Am. Chem. Soc. 145 (2023) 11323–11332.

[71] D. Wakerley, S. Lamaison, F. Ozanam, N. Menguy, D. Mercier, P. Marcus, M. Fontecave, V. Mougel, Bio-inspired hydrophobicity promotes CO2 reduction on a Cu surface, Nat. Mater. 18 (2019) 1222–1227.

[72] F.P.G. de Arquer, C.T. Dinh, A. Ozden, J. Wicks, C. McCallum, A.R. Kirmani, D. H. Nam, C. Gabardo, A. Seifitokaldani, X. Wang, Y.G.C. Li, F.W. Li, J. Edwards, L. J. Richter, S.J. Thorpe, D. Sinton, E.H. Sargent, CO2 electrolysis to multicarbon products at activities greater than 1 A cm-2, Science 367 (2020) 661–666.

[73] C.T. Dinh, T. Burdyny, M.G. Kibria, A. Seifitokaldani, C.M. Gabardo, F.P.G. de Arquer, A. Kiani, J.P. Edwards, P. De Luna, O.S. Bushuyev, C.Q. Zou, R. Quintero-Bermudez, Y.J. Pang, D. Sinton, E.H. Sargent, CO2 electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface, Science 360 (2018) 783–787.

[74] R. Chen, W. Tian, Y. Jia, W. Xu, F. Chen, X. Duan, Q. Xie, C. Hu, W. Liu, Y. Zhao, Y. Kuang, Y. Zhang, X. Sun, Engineering interfacial aerophilicity of nickel-embedded nitrogen-doped CNTs for electrochemical CO2 reduction, ACS Appl. Energy Mater. 2 (2019) 3991–3998.

[75] M. Zhang, T. Zhao, C. Yu, Q. Liu, G. Wang, H. Yang, M. Yang, L. Jiang, M. Liu, Amphiphilic Pd@micro-organohydrogels with controlled wettability for enhancing gas-liquid-solid triphasic catalytic performance, Nano Res. 15 (2021) 557–563.

[76] B. Yi, Y.-L. Wong, K. Li, C. Hou, T. Ma, Z. Xu, X. Yao, Highly catalytic metal-organic framework coating enabled by liquid superwetting and confinement, Nano Res. 16 (2022) 7716–7723.

[77] L. Xue, X. Wu, Y. Liu, B. Xu, X. Wang, S. Dai, P. Liu, H. Yang, Hydrophobic 1-octadecanethiol functionalized copper catalyst promotes robust high-current CO2 gas-diffusion electrolysis, Nano Res 15 (2021) 1393–1398.

[78] Y. Li, P. Hasin, Y. Wu, NixCo3−xO4 nanowire arrays for electrocatalytic oxygen evolution, Adv. Mater. 22 (2010) 1926–1929.

[79] M. Liu, Y. Pang, B. Zhang, P. De Luna, O. Voznyy, J. Xu, X. Zheng, C.T. Dinh, F. Fan, C. Cao, F.P. de Arquer, T.S. Safaei, A. Mepham, A. Klinkova, E. Kumacheva, T. Filleter, D. Sinton, S.O. Kelley, E.H. Sargent, Enhanced electrocatalytic CO2 reduction via field-induced reagent concentration, Nature 537 (2016) 382–386.

[80] H. Mistry, F. Behafarid, R. Reske, A.S. Varela, P. Strasser, B. Roldan Cuenya, Tuning catalytic selectivity at the mesoscale via interparticle interactions, ACS Catal. 6 (2016) 1075–1080.

[81] Y. Yoon, A.S. Hall, Y. Surendranath, Tuning of silver catalyst mesostructure promotes selective carbon dioxide conversion into fuels, Angew. Chem. Int. Ed. Engl. 55 (2016) 15282–15286.

[82] S.S. Latthe, C. Terashima, K. Nakata, A. Fujishima, Superhydrophobic surfaces developed by mimicking hierarchical surface morphology of lotus leaf, Molecules 19 (2014) 4256–4283.

[83] K.S. Liu, L. Jiang, Bio-inspired self-cleaning surfaces, in: D.R. Clarke (Ed.) Annu. Rev. Mater. Res., 42(2012), 231–263.

[84] X. Liu, M. Wei, Q. Wang, Y. Tian, J. Han, H. Gu, H. Ding, Q. Chen, K. Zhou, Z. Gu, Capillary-force-driven self-assembly of 4D-rinted microstructures, Adv. Mater. 33 (2021), e2100332.

[85] P. Fu, H. Li, J. Gong, Z. Fan, A.T. Smith, K. Shen, T.O. Khalfalla, H. Huang, X. Qian, J.R. McCutcheon, L. Sun, 4D printing of polymers: Techniques, materials, and prospects, Prog. Polym. Sci. 126 (2022), 101506.

[86] L.M. Pegram, M.T. Record, Hofmeister salt effects on surface tension arise from partitioning of anions and cations between bulk water and the air-water interface, J. Phys. Chem. B 111 (2007) 5411–5417.

[87] Z. Ma, Z. Yang, W. Lai, Q. Wang, Y. Qiao, H. Tao, C. Lian, M. Liu, C. Ma, A. Pan, H. Huang, CO2 electroreduction to multicarbon products in strongly acidic electrolyte via synergistically modulating the local microenvironment, Nat. Commun. 13 (2022) 7596.

[88] P. De Luna, R. Quintero-Bermudez, C.-T. Dinh, M.B. Ross, O.S. Bushuyev, P. Todorović, T. Regier, S.O. Kelley, P. Yang, E.H. Sargent, Catalyst electro-redeposition controls morphology and oxidation state for selective carbon dioxide reduction, Nat. Catal. 1 (2018) 103–110.

[89] H. Mistry, A.S. Varela, C.S. Bonifacio, I. Zegkinoglou, I. Sinev, Y.W. Choi, K. Kisslinger, E.A. Stach, J.C. Yang, P. Strasser, B.R. Cuenya, Highly selective plasma-activated copper catalysts for carbon dioxide reduction to ethylene, Nat. Commun. 7 (2016) 12123.

[90] A. Eilert, F.S. Roberts, D. Friebel, A. Nilsson, Formation of Copper catalysts for CO2 reduction with high ethylene/methane product ratio investigated with In situ X-ray absorption spectroscopy, J. Phys. Chem. Lett. 7 (2016) 1466–1470.

[91] H. Mistry, Y.W. Choi, A. Bagger, F. Scholten, C.S. Bonifacio, I. Sinev, N.J. Divins, I. Zegkinoglou, H.S. Jeon, K. Kisslinger, E.A. Stach, J.C. Yang, J. Rossmeisl, B. Roldan Cuenya, Enhanced carbon dioxide electroreduction to carbon monoxide over defect-rich plasma-activated Silver catalysts, Angew. Chem. Int. Ed. Engl. 56 (2017) 11394–11398.

[92] B.L. Mehdi, J. Qian, E. Nasybulin, C. Park, D.A. Welch, R. Faller, H. Mehta, W. A. Henderson, W. Xu, C.M. Wang, J.E. Evans, J. Liu, J.G. Zhang, K.T. Mueller, N. D. Browning, Observation and quantification of nanoscale processes in lithium batteries by operando electrochemical (S)TEM, Nano Lett. 15 (2015) 2168–2173.

[93] N. Hodnik, G. Dehm, K.J. Mayrhofer, Importance and challenges of electrochemical in situ liquid cell electron microscopy for energy conversion research, Acc. Chem. Res. 49 (2016) 2015–2022.

[94] T. Kai, C.G. Zoski, A.J. Bard, Scanning electrochemical microscopy at the nanometer level, Chem. Commun. (Camb.). 54 (2018) 1934–1947.

[95] K. Ye, G. Zhang, X.-Y. Ma, C. Deng, X. Huang, C. Yuan, G. Meng, W.-B. Cai, K. Jiang, Resolving local reaction environment toward an optimized CO2-to-CO conversion performance, Energy Environ. Sci. 15 (2022) 749–759.

[96] M. Favaro, B. Jeong, P.N. Ross, J. Yano, Z. Hussain, Z. Liu, E.J. Crumlin, Unravelling the electrochemical double layer by direct probing of the solid/liquid interface, Nat. Commun. 7 (2016) 12695.

[97] X. Zhang, A.J. Rowberg, N. Govindarajan, X. He, Hydrogen bond network at the H2O/solid interface, Encycl. Solid-Liq. Interfaces (2023).

[98] S. Axnanda, E.J. Crumlin, B. Mao, S. Rani, R. Chang, P.G. Karlsson, M.O. Edwards, M. Lundqvist, R. Moberg, P. Ross, Z. Hussain, Z. Liu, Using "Tender" X-ray ambient pressure X-ray photoelectron spectroscopy as a direct robe of solid-liquid interface, Sci. Rep. 5 (2015) 9788.

[99] A. Kolmakov, D.A. Dikin, L.J. Cote, J. Huang, M.K. Abyaneh, M. Amati, L. Gregoratti, S. Gunther, M. Kiskinova, Graphene oxide windows for in situ

environmental cell photoelectron spectroscopy, Nat. Nanotechnol. 6 (2011) 651–657.

[100] R.S. Weatherup, 2D mmaterial membranes for operando atmospheric pressure photoelectron spectroscopy, Top. Catal. 61 (2018) 2085–2102.

[101] J.J. Velasco-Velez, V. Pfeifer, M. Havecker, R.S. Weatherup, R. Arrigo, C. H. Chuang, E. Stotz, G. Weinberg, M. Salmeron, R. Schlogl, Photoelectron spectroscopy at the graphene-liquid interface reveals the electronic structure of an electrodeposited Cobalt/Graphene electrocatalyst, Angew. Chem. Int. Ed. Engl. 54 (2015) 14554–14558.

[102] Y. Yu, A. Baskin, C. Valero-Vidal, N.T. Hahn, Q. Liu, K.R. Zavadil, B.W. Eichhorn, D. Prendergast, E.J. Crumlin, Instability at the electrode/electrolyte interface induced by hard cation chelation and nucleophilic attack, Chem. Mater. 29 (2017) 8504–8512.

[103] H.S. Casalongue, S. Kaya, V. Viswanathan, D.J. Miller, D. Friebel, H.A. Hansen, J. K. Nørskov, A. Nilsson, H. Ogasawara, Direct observation of the oxygenated species during oxygen reduction on a platinum fuel cell cathode, Nat. Commun. 4 (2013) 2817.

[104] R. Arrigo, M. Havecker, M.E. Schuster, C. Ranjan, E. Stotz, A. Knop-Gericke, R. Schlogl, In situ study of the gas-phase electrolysis of water on platinum by NAP-XPS, Angew. Chem. Int. Ed. Engl. 52 (2013) 11660–11664.

[105] Y.H. Lu, J.M. Larson, A. Baskin, X. Zhao, P.D. Ashby, D. Prendergast, H.A. Bechtel, R. Kostecki, M. Salmeron, Infrared nanospectroscopy at the graphene-electrolyte interface, Nano Lett. 19 (2019) 5388–5393.

[106] Y.H. Lu, C. Morales, X. Zhao, M.A. van Spronsen, A. Baskin, D. Prendergast, P. Yang, H.A. Bechtel, E.S. Barnard, D.F. Ogletree, V. Altoe, L. Soriano, A. M. Schwartzberg, M. Salmeron, Ultrathin free-standing oxide membranes for electron and photon spectroscopy studies of solid-gas and solid-liquid interfaces, Nano Lett. 20 (2020) 6364–6371.

[107] V.A. Saveleva, E.R. Savinova, Insights into electrocatalysis from ambient pressure photoelectron spectroscopy, Curr. Opin. Electrochem. 17 (2019) 79–89.

[108] E.A. Carbonio, J.-J. Velasco-Velez, R. Schlögl, A. Knop-Gericke, Perspective—outlook on operando photoelectron and absorption spectroscopy to probe catalysts at the solid-liquid electrochemical interface, J. Electrochem. Soc. 167 (2020), 054509.

[109] P. Lukas, N. Rachel, B. Sebastian, H. Caroline, K. Gudrun, S. Robert, T. Sven, G. Mark, Inelastic electron scattering by the gas phase in near ambient pressure XPS measurements, surface and interface analysis: SIA: An international journal devoted to the development and application of techniques for the analysis of surfaces, Interfaces Thin Films 53 (2021) 605–617.

[110] H. Li, X. Qin, T. Jiang, X.Y. Ma, K. Jiang, W.B. Cai, Changing the product selectivity for electrocatalysis of CO_2 reduction reaction on plated Cu electrodes, ChemCatChem 11 (2019) 6139–6146.

[111] Y. Kim, S. Park, S.-J. Shin, W. Choi, B.K. Min, H. Kim, W. Kim, Y.J. Hwang, Time-resolved observation of C–C coupling intermediates on Cu electrodes for selective electrochemical CO_2 reduction, Energy Environ. Sci. 13 (2020) 4301–4311.

[112] R. Yang, L. Mei, Y. Fan, Q. Zhang, H.G. Liao, J. Yang, J. Li, Z. Zeng, Fabrication of liquid cell for in situ transmission electron microscopy of electrochemical processes, Nat. Protoc. 18 (2022) 555–578.

[113] S. Mildner, M. Beleggia, D. Mierwaldt, T.W. Hansen, J.B. Wagner, S. Yazdi, T. Kasama, J. Ciston, Y. Zhu, C. Jooss, Environmental TEM study of electron beam induced electrochemistry of $Pr_{0.64}Ca_{0.36}MnO_3$ catalysts for oxygen evolution, J. Phys. Chem. C 119 (2015) 5301–5310.

[114] Y. Liang, J.H.K. Pfisterer, D. McLaughlin, C. Csoklich, L. Seidl, A.S. Bandarenka, O. Schneider, Electrochemical scanning probe microscopies in electrocatalysis, Small Methods 3 (2019) 1800387.

[115] C.L. Bentley, M. Kang, P.R. Unwin, Nanoscale surface structure-activity in electrochemistry and electrocatalysis, J. Am. Chem. Soc. 141 (2019) 2179–2193.

[116] E. Fahrenkrug, D.H. Alsem, N. Salmon, S. Maldonado, Electrochemical measurements in in situ TEM experiments, J. Electrochem. Soc. 164 (2017) H358–H364.

[117] T. Zhang, S. Li, Y. Du, T. He, Y. Shen, C. Bai, Y. Huang, X. Zhou, Revealing the activity distribution of a single nanocatalyst by locating single nanobubbles with super-resolution microscopy, J. Phys. Chem. Lett. 9 (2018) 5630–5635.

[118] Y.J. Kim, A. Lim, J.M. Kim, D. Lim, K.H. Chae, E.N. Cho, H.J. Han, K.U. Jeon, M. Kim, G.H. Lee, G.R. Lee, H.S. Ahn, H.S. Park, H. Kim, J.Y. Kim, Y.S. Jung, Highly efficient oxygen evolution reaction via facile bubble transport realized by three-dimensionally stack-printed catalysts, Nat. Commun. 11 (2020) 4921.

[119] Y. Li, H. Zhang, T. Xu, Z. Lu, X. Wu, P. Wan, X. Sun, L. Jiang, Under-water superaerophobic pine-shaped Pt nnanoarray electrode for ultrahigh-performance hydrogen evolution, Adv. Funct. Mater. 25 (2015) 1737–1744.

[120] W.A. Yin, Y.T. Cai, L.B. Xie, H. Huang, E.C. Zhu, J.A. Pan, J.Q. Bu, H. Chen, Y. Yuan, Z.C. Zhuang, L.L. Wang, Revisited electrochemical gas evolution reactions from the perspective of gas bubbles, Nano Res. 4 (2023) 4381–4398.

[121] E.L. Clark, J. Resasco, A. Landers, J. Lin, L.-T. Chung, A. Walton, C. Hahn, T. F. Jaramillo, A.T. Bell, Standards and protocols for data acquisition and reporting for studies of the electrochemical reduction of carbon dioxide, ACS Catal. 8 (2018) 6560–6570.

[122] V.R. Stamenkovic, D. Strmcnik, P.P. Lopes, N.M. Markovic, Energy and fuels from electrochemical interfaces, Nat. Mater. 16 (2016) 57–69.

[123] M.L. Perry, J. Newman, E.J. Cairns, Mass transport in gas-diffusion electrodes: a diagnostic tool for fuel-cell cathodes, J. Electrochem. Soc. 145 (1998) 5–15.

[124] D. Higgins, C. Hahn, C. Xiang, T.F. Jaramillo, A.Z. Weber, Gas-diffusion electrodes for carbon dioxide reduction: a new paradigm, ACS Energy Lett. 4 (2018) 317–324.

[125] J. Qin, D. Zhou, B. Shi, F. Chen, L. Luo, A. Kumar, C. Wang, X. Lin, S. Sheng, W. Xu, Z. Shang, C. Cheng, Y. Kuang, W.F. Lin, H. Xu, X. Sun, Understanding of dynamic contacting behaviors of underwater gas bubbles on solid surfaces, Langmuir 36 (2020) 11422–11428.

[126] C. Sun, L. Wang, W. Zhao, L. Xie, J. Wang, J. Li, B. Li, S. Liu, Z. Zhuang, Q. Zhao, Atomic-level design of active site on two-dimensional MoS_2 toward efficient hydrogen evolution: Experiment, theory, and artificial intelligence modelling, Adv. Funct. Mater. 32 (2022) 2206163.

[127] X. Wang, J.F. de Araujo, W. Ju, A. Bagger, H. Schmies, S. Kuhl, J. Rossmeisl, P. Strasser, Mechanistic reaction pathways of enhanced ethylene yields during electroreduction of CO_2-CO co-feeds on Cu and Cu-tandem electrocatalysts, Nat. Nanotechnol. 14 (2019) 1063–1070.

[128] J. Hao, S. Xie, Q. Huang, Z. Ding, H. Sheng, C. Zhang, J. Yao, Spin-enhanced C–C coupling in CO_2 electroreduction with oxide-derived Copper, CCS Chem. 0 (2022) 1–13.

[129] M. Orlik, K. Doblhofer, G. Ertl, On the mechanism of electrohydrodynamic convection in thin-layer electrolytic cells, J. Phys. Chem. B 102 (1998) 6367–6374.

[130] H. Wang, L. Pilon, Accurate simulations of electric double layer capacitance of ultramicroelectrodes, J. Phys. Chem. C 115 (2011) 16711–16719.

[131] X. Qin, T. Vegge, H.A. Hansen, Cation-coordinated inner-sphere CO_2 electroreduction at Au-Water interfaces, J. Am. Chem. Soc. 145 (2023) 1897–1905.

[132] R. Kortlever, J. Shen, K.J. Schouten, F. Calle-Vallejo, M.T. Koper, Catalysts and reaction pathways for the electrochemical reduction of carbon dioxide, J. Phys. Chem. Lett. 6 (2015) 4073–4082.

[133] A. Bajpai, K. Frey, W.F. Schneider, Comparison of coverage-dependent binding energy models for mean-field microkinetic rate predictions, Langmuir 36 (2020) 465–474.

[134] F. Tao, S. Dag, L.-W. Wang, Z. Liu, D.R. Butcher, H. Bluhm, M. Salmeron, G. A. Somorjai, Break-up of stepped platinum catalyst surfaces by high CO coverage, Science 327 (2010) 850–853.

[135] F. Tao, M. Salmeron, In situ studies of chemistry and structure of materials in reactive environments, Science 331 (2011) 171–174.

[136] Y. Huang, A.D. Handoko, P. Hirunsit, B.S. Yeo, Electrochemical reduction of CO_2 using Copper single-crystal surfaces: Effects of CO* coverage on the selective formation of ethylene, ACS Catal. 7 (2017) 1749–1756.

[137] K.P. Kuhl, T. Hatsukade, E.R. Cave, D.N. Abram, J. Kibsgaard, T.F. Jaramillo, Electrocatalytic conversion of carbon dioxide to methane and methanol on transition metal surfaces, J. Am. Chem. Soc. 136 (2014) 14107–14113.

[138] K.P. Kuhl, E.R. Cave, D.N. Abram, T.F. Jaramillo, New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces, Energy Environ. Sci. 5 (2012) 7050–7059.

[139] C. Wang, C. Zhu, M. Zhang, Y. Geng, Z. Su, Copper dimer anchored in g-CN monolayer as an efficient electrocatalyst for CO_2 reduction reaction: a computational study, Adv. Theory Simul. 3 (2020), 2000218.

[140] S. Jin, Z. Hao, K. Zhang, Z. Yan, J. Chen, Advances and challenges for the electrochemical reduction of CO_2 to CO: From fundamentals to industrialization, Angew. Chem. Int. Ed. Engl. 60 (2021) 20627–20648.

[141] D. Kim, J. Resasco, Y. Yu, A.M. Asiri, P. Yang, Synergistic geometric and electronic effects for electrochemical reduction of carbon dioxide using gold-copper bimetallic nanoparticles, Nat. Commun. 5 (2014) 4948.

[142] S. Yu, A.J. Wilson, G. Kumari, X. Zhang, P.K. Jain, Opportunities andchallenges of solar-energy-driven carbon dioxide to fuel conversion with plasmonic catalysts, ACS Energy Lett. 2 (2017) 2058–2070.

[143] Y. Lei, Z. Wang, A. Bao, X. Tang, X. Huang, H. Yi, S. Zhao, T. Sun, J. Wang, F. Gao, Recent advances on electrocatalytic CO_2 reduction to resources: Target products, reaction pathways and typical catalysts, Chem. Eng. J. 453 (2023), 139663.

[144] W. Gong, J. Stearnes, D. Fornasiero, R.A. Hayes, J. Ralston, The influence of dissolved gas on the interactions between surfaces of different hydrophobicity in aqueous media Part II. A spectroscopic study, Phys. Chem. Chem. Phys. 1 (1999) 2799–2803.

[145] K. Ikeue, H. Yamashita, M. Anpo, T. Takewaki, Photocatalytic reduction of CO_2 with H_2O on Ti−β zeolite photocatalysts: Effect of the hydrophobic and hydrophilic properties, J. Phys. Chem. B 105 (2001) 8350–8355.

[146] H. Yamashita, K. Ikeue, T. Takewaki, M. Anpo, In situ XAFS studies on the effects of the hydrophobic–hydrophilic properties of Ti-Beta zeolites in the photocatalytic reduction of CO_2 with H_2O, Top. Catal. 18 (2002) 95–100.

[147] K. Ikeue, S. Nozaki, M. Ogawa, M. Anpo, Photocatalytic reduction of CO_2 with H_2O on Ti-containing porous silica thin film photocatalysts, Catal. Lett. 80 (2002) 111–114.

[148] H.-C. Yeh, R.-J. Yang, W.-J. Luo, J.-Y. Jiang, Y.-D. Kuan, X.-Q. Lin, The performance analysis of direct methanol fuel cells with different hydrophobic anode channels, J. Power Sources 196 (2011) 270–278.

[149] C. Dong, M. Xing, J. Zhang, Economic hydrophobicity triggering of CO_2 photoreduction for selective CH_4 generation on noble-metal-free TiO_2-SiO_2, J. Phys. Chem. Lett. 7 (2016) 2962–2966.

[150] C.X. Zhao, Y.F. Bu, W. Gao, Q. Jiang, CO_2 reduction mechanism on the Pb(111) surface: Effect of solvent and cations, J. Phys. Chem. C 121 (2017) 19767–19773.

[151] L.-H. Xie, M.-M. Xu, X.-M. Liu, M.-J. Zhao, J.-R. Li, Hydrophobic metal–organic frameworks: assessment, construction, and diverse applications, Adv. Sci. 7 (2020) 1901758.

[152] H. Rabiee, L. Ge, J. Zhao, X. Zhang, M. Li, S. Hu, S. Smart, T.E. Rufford, Z. Zhu, H. Wang, Z. Yuan, Regulating the reaction zone of electrochemical CO_2 reduction on gas-diffusion electrodes by distinctive hydrophilic-hydrophobic catalyst layers, Appl. Catal. B 310 (2022), 121362.

[153] D. Zeng, C. Li, W. Wang, L. Zhang, Y. Zhang, J. Wang, L. Zhang, X. Zhou, W. Wang, Insights into the hydrophobic surface promoting electrochemical CO_2 reduction to ethylene, Chem. Eng. J. 461 (2023), 142133.